OPTIMIZATION OF RHODAMINE B DYE REMOVAL FROM AQUEOUS SOLUTIONS BY LIQUID-LIQUID EXTRACTION

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OPTIMIZATION OF RHODAMINE B DYE REMOVAL FROM AQUEOUS SOLUTIONS BY LIQUID-LIQUID EXTRACTION

by

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TABLE OF CONTENTS

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: MATERIALS AND METHODS

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

D	Distribution coefficient
$[Dye]_{ini}$	Initial dye concentration in the aqueous phase
$[Dye]_{aq}$	Dye concentration of aqueous phase after extraction
$[Dye]_{org}$	Dye concentration in the organic phase
$[Dye]_{i,F}$	Initial dye concentration in the aqueous phase
$[Dye]_{f,F}$	Final dye concentration of aqueous phase after extraction
$[Dye]_{f,S}$	Final dye concentration of stripping phase after stripping
F-test	Fisher's test
H_0	Null hypothesis
HCl	Hydrochloric acid
H_2SO_4	Sulfuric acid
k	Number of factor
n	Number of replicate factor
n_C	Number of center points
n_F	Number of factorial points
$n-p$	Degree of freedom associated whit the error sum of squares
$n-1$	Degree of freedom associated with total sum of squares
NaOH	Sodium hydroxide
O/A	Organic phase/ Aqueous phase
OH·	Hydroxyl radicals
P-value	Probability
p	Fraction size of full factorial design
R^2	Determination coefficient
R^2_{adj}	Adjusted R^2
R^2_{pre}	Predicted R^2
SD	Standard deviation

RSD	Relative standard deviation
SS_T	Total sum of squares
SS_R	The residual sum of squares
SS_E	The error sum of squares
t-stat	t-statistics
$\bar{x}$	Average deviation
x_j	Independent variable
x_i	Independent variable
y_{ij}	The *ij*th observation

α	Distance between the center points in CCD
β_0	Intercept of the plan
β_j	Regression coefficient
β_{jj}	Pure second-order or quadratic effects
β_{ij}	Interaction term
μ	The overall mean
τ_i	The *i*th treatment effect

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
BOD	Biochemical oxygen demand
BLM	Bulk liquid membrane
CCD	Central composite design
COD	Chemical oxygen demand
DOE	Design of experiments
ELM	Emulsion of membrane
F	Feed
LLE	Liquid-liquid extraction
M	Membrane
MUFA	Monounsaturated fatty acid
PUFA	Polyunsaturated fatty acid
RSM	Response surface methodology
RB	Rhodamine B
S	Strip
SD	Standard division
SFA	Saturated fatty acid
SLM	Supported liquid membrane
TAG	Triacylglycerol
TBP	Tributylphophate

PENGOPTIMUMAN PELUCUTAN PEWARNA RHODAMINE B DARIPADA LARUTAN AKUES SECARA PENGEKSTRAKAN CECAIR-CECAIR

ABSTRAK

Perindustrian yang pesat dan intensif telah menjana jumlah sisa akueus yang mengandungi pelbagai jenis bahan kimia seperti sisa pewarna. Rhodamine B (RB) adalah sangat larut dalam air dan pelarut organik, serta berwarna neon biru-merah. Ia juga telah dianggap sebagai toksik dan berpotensi karsinogen. Dalam kajian ini, RB telah diekstrak dengan menggunakan minyak sayuran sebagai bahan kimia organik. Membran cecair (LM) adalah sistem pemisahan berdasarkan prinsip pengekstrakan cecair-cecair pengekstrakan (LLE) yang menggabungkan pengekstrakan pelarut dan proses pelucutan dalam satu langkah。Kajian ini bertujuan untuk: a) Untuk memilih sayur-sayuran sesuai berasaskan minyak pelarut organik untuk pelucutan RB; b) untuk mengoptimumkan faktor (pH, berjabat masa, gegaran kelajuan dan organik ke fasa akueus (O / A) nisbah) yang memberi kesan pengekstrakan RB menggunakan pelarut organik berasaskan minyak sayur-sayuran; c) untuk memilih ejen pelucutan untuk RB pelucutan daripada pelarut organik berasaskan minyak sayur-sayuran; d) untuk mengkaji kesan kelikatan pada pengekstrakan RB. Kelikatan minyak kacang soya dan minyak jagung telah diukur. Minyak kacang soya mempunyai kelikatan yang rendah (45.16cP) berbanding dengan minyak jagung (51.95cP) dan ia juga mencatatkan penggunaan global kedua tertinggi pada dekad yang lalu. Pemeriksaan 4

faktor (pH, nisbah O/A, kelajuan gegaran dan masa gegaran) yang mempengaruhi peratus pengekstrakan (pelucutan warna) menggunakan minyak kacang soya sebagai pelarut organik dengan reka bentuk faktorial dua tingkat mendedahkan hanya pH, nisbah O/A dan interaksi antara mereka dianggap signifikan. Satu reka bentuk komposit pusat telah dibina untuk mengoptimumkan dua faktor (pH dan nisbah fasa organik kepada fasa akueus) dalam pengekstrakan RB. Model regresi telah dijanakan untuk pengiraan peratus pengekstrakan manakala R^2_{adj} (0.9600) dan R^2 (0,9767) telah ditentukan. Keadaan optimum diramalkan oleh model tersebut adalah pH 3.42 dan nisbah O/A 1.1. Nilai eksperimen bagi peratus pelucutan warna (95.74%) diperolehi dalam keadaan optimum adalah selari dengan peratus pelucutan warna yang diramalkan (96.14%) dengan factor bahagian sebanyak 0.4%. 1M asid hidroklorik telah dipilih sebagai ejen pelucutan kerana peratus pelucutannya yang lebih tinggi berbanding dengan asid sulfurik. Dalam keadaan optimum, minyak kacang soya dan campuran kerosin dan minyak kacang soya telah dipilih sebagai pelarut organik untuk mengkaji kesan kelikatan pada pengekstrakan RB dan pelucutan dengan membina sistem lapisan cecair pukal. peratus pengekstrakan dan peratus pelucutan RB telah dikira melalui penilaian kepekatan pewarna. Sepanjang 20h, peratus pengekstrakan mencapai nilai yang tertinggi iaitu 95.4% dengan menggunakan campuran 10% kesorin dan 90% minyak kacang soya sebagai pelarut organik (kelikatan 32.99cP) manakala % pengekstrakan mencatat sebanyak 93.5% dengan menggunakan 10% kerosin dan 90% minyak kacang soya sebagai pelarut organik (kelikatan 45.16cP) dan peratus pengekstrakan dengan menggunakan 5% kerosin dan

95% minyak kacang soya adalah 94.2% (kelikatan 40.83cP). Nilai peratus pelucutan adalah sama dengan peratus pengekstrakan. Kesimpulannya, kelikatan yang lebih rendah (campuran kerosin dan minyak kacang soya sebagai lapisan organik) akan meningkatkan kadar pemindahan manakala kelikatan pelarut organik yang lebih tinggi akan mengurangkan kadarnya.

OPTIMIZATION OF RHODAMINE B DYE REMOVAL FROM AQUEOUS SOLUTIONS BY LIQUID-LIQUID MEMBRANE

ABSTRACT

Rapid and intensive industrialization has generated large volumes of aqueous wastes containing various chemicals such as dye waste. Rhodamine B (RB) is highly soluble in water and organic solvent, and its color is fluorescent bluish-red. It has also been regarded as toxic and potentially carcinogenic. In this research, RB was extracted by using vegetable oil as organic chemical. Liquid membrane (LM) is a separation system based on the principle of liquid-liquid extraction (LLE) which combines the solvent extraction and stripping processes in a single step. This research is aimed to: a) To select a suitable vegetable oil-based organic solvent for RB extraction; b) to optimize the factors (pH, shaking time, shaking speed and organic to aqueous phase (O/A) ratio) affecting RB extraction using vegetable-oil-based organic solvent; c) to select a stripping agent for RB stripping from vegetable oil-based organic solvent; d) to investigate the effect of viscosity on extraction of RB. Vegetable oils were used to replace the petroleum-based organic solvents and the influence of viscosity on rhodamine B transfer was investigated. LLE results indicate that soybean oil has relatively lower viscosity (45.16cP) compared with corn oil (51.95cP) and hydrochloric acid were the most suitable organic solvent and stripping agents for RB extraction and stripping. Screening of 4 factors (pH, O/A ratio, shaking speed and shaking time) influencing the RB

extraction by soybean oil as organic solvent using a two-level factorial design reveals, only pH, O/A ratio and their interactions are considered as significant terms. A central composite design was built to optimize the two factors (pH and ratio of organic phase to aqueous phase) in the extraction of RB. A regression model was developed for percent extraction while R^2_{adj} (0.9600) and R^2 (0.9767) were determined. The optimum condition predicted by the model which is: pH of 3.42 and O/A ratio of 1.1, respectively. The experimental value of percent color removal (95.74%) is obtained under the optimum condition, which is comparable with the predicted percent color removal (96.14%) with a division of 0.4%. 1M hydrochloric acid was selected as stripping agent as its higher percent stripping compared with sulfuric acid. Under the optimized condition, soybean oil and the mixture of kerosene and soybean oil were selected as the organic solvent respectively to investigate the influence of viscosity on RB extraction and stripping by building a bulk liquid membrane system. The percent extraction and percent stripping of RB was calculated according to the measurement of dye concentration by time. At 20h of conducting time, the percent extraction reached its highest value of 95.4% by using the mixture of 10% kerosene with 90% soybean oil as organic solvents (viscosity of 32.99cP) while the percent extraction is 93.5% by using 10% kerosene with 90% soybean oil as organic solvent (viscosity of 45.16cP) and percent extraction by using 5% kerosene with 95% soybean oil as organic solvent is 94.2% (viscosity of 40.83cP). The result of percent stripping is parallel to % extraction. As a conclusion, lower viscosity (mixture of kerosene and soybean oil as organic membrane) will increase

the transfer rate while higher viscosity of the organic solvent will decrease it.

CHAPTER 1

INTRODUCTION

1.0 Overview

This chapter is aimed to give an overview of the research background. It covers an introduction of dye wastewater, the common treatment techniques of dye-containing wastewater and a need of greener treatment techniques for Rhodamine B (RB). The objectives of this research are also presented.

1.1 Dye Wastewater

Nowadays, water demand is increasing twice as fast with the growth of human population and water pollution by metals or organic materials has become a major concern that threaten humanity. Dyes are one kind of organic materials which are widely used in textile and industrial production. Discharge of dye wastewater is harmful to the living creatures and environment. There are approximately 700,000 tons of dyes and pigments consumed globally and 5000 tons of dying materials are discharged to the environment every year (Pirkarami & Olya, 2013). This is due to a large increasing demand of dye materials by textile merchandises and the productions capacity of textile industries. Based on the source, dyes can be classified into two categories: natural dyes and synthetic dyes. Most natural dyes are unstable, hence synthetic dyes are becoming an essential alternative. Among the synthetic dyes, azo dyes have the largest amount of dyes widely used in various industries due to its simple

synthesis process. The effluents containing azo dyes are usually heavily colored, concentrated with salt and have high values of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) (Tung et al., 2016). It is very important to treat dye wastewater due to their characteristics such as stable, colorant, stubborn, toxic (Han et al., 2016). Many dyes used in by textile industry are also potentially carcinogenic because the chemicals used to manufacture synthetic dyes such as benzene, chlorine and other compounds (Colditz, 2007). Discharge of dye wastes into receiving streams will affect both the aesthetic nature and the transmission of sunlight into streams therefore will reduce photosynthetic activity (Shibangi et al., 2013)

1.2 Treatment Techniques for Dye Wastewater

Dye wastewater treatment techniques can be classified into few categories: physical (adsorption, membrane filtration, irradiation, etc.), chemical (ozonation, advanced oxidation processes (AOPs), etc.), biological and electrochemical treatment. The physical methods usually require secondary treatment since the treatment techniques are usually non-destructive and the pollutants are merely transferred from one medium to another. Chemical methods have relatively high economically cost due to high dosage used of materials in the treatment and the disposal of large quantity of sludge (Muthuraman & Teng, 2012). In order to remove all the contaminants present in the wastewater, the use of a combination of different methods of dye treatment is considered to be necessary in most situations. Therefore, adsorption became one of the most effective methods to remove color from textile wastewater (Sivamani & Leena,

2009).

1.2.1 Adsorption

The adsorption treatment offers a good potential for removing dyes from the industrial wastewater. The adsorbent includes the activated carbon (Regti et al., 2016), citric acid (Li et al., 2012) activated alumina (Wasti & Awan, 2016), bagasse (Valix et al., 2004) banana peel (Annadurai et al., 2002) and other. The advantages of this technique is relatively low cost with a simple design, easy operation and insensitive toxic substances (Gisi et al., 2016).

1.2.2 Irradiation

The principle of irradiation the treatment by using electron beams or gamma rays. This treatment is simple, effective and it also can be used to eliminate various types organic pollutant and disinfect the harmful microorganisms (Borely et al., 1998).

1.2.3 Ozonation

Ozonation has two principle mechanisms are a) direct reaction where molecular ozone reacts with organic contaminants directly b) indirect reaction where organic pollutants are oxidized by highly reactive free radicals derives from decomposition of molecular ozone (Fanchiang & Tseng, 2009). The technique of ozonation will not produce sludge hence reduce the cost of the treatment (Poznyak et al., 2007).

1.2.4 Advanced Oxidation Processes (AOPs)

AOPs is based on the oxidation processes involving to generate the sufficient quantity of hydroxyl radicals (OH·) to effect water purification (Deng & Zhao, 2015). The advantages of AOPs are high surface loading tolerance level, ease of operation, high efficiency, high removal of COD and less sludge (Dehghani et al., 2016).

1.2.5 Biological Treatment

Biological treatments include aerobic treatment, anaerobic treatment and aerobic-anaerobic combined treatment. It requires less energy and chemicals compared to the physical and chemical treatment and it can provide a high percentage of COD (chemical oxygen demand) and BOD (biochemical oxygen demand) reduction. However, the biological treatments still achieve a poor removal of color (Lopez et al., 2000).

1.2.6 Electrochemical Treatment

The principle of electrochemical treatment is stimulating the reaction by adding oxidizing agents. On the good side, the breakdown components are generally non-toxic. However, the study of electrochemical treatment is not always related to the application and the surface treatment of diamond electrode in the water treatment application is even considered lack of necessary (Chen et al., 2016).

1.3 Liquid Membrane

Liquid Membrane is a separation system consisting of liquid film through which selective mass transfer of ions or molecules occurs via permeation and transport process. It has some advantages of selectivity, a cost reducing potential and renewable carrier. However, the toxicity of the organic carrier is the problem need to overcome (Muthuraman & Palanibelu, 2006). There are three types of liquid membrane: bulk liquid membrane (BLM), supported liquid membrane (SLM), and emulsion liquid membrane (ELM) (Khani et al., 2015) and (Ramkumar & Chanhramouleeswaran, 2015). BLM and SLM do not involve phase separation, however ELM involves phase separation. Figure 1.1 shows the typical BLM, SLM and ELM.

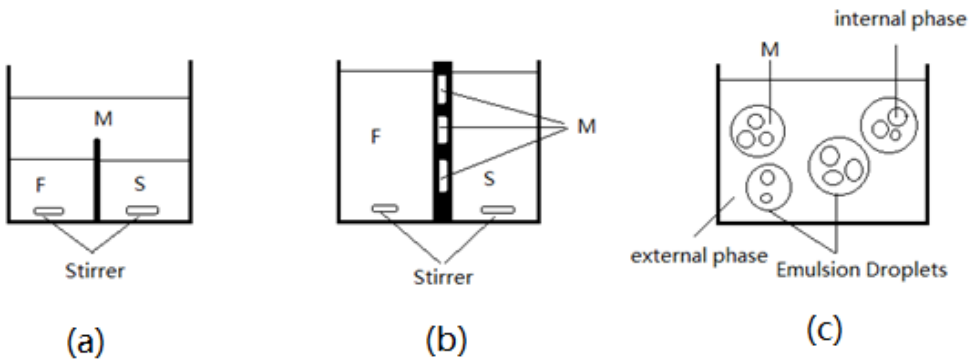

Figure 1.1 Schematic diagrams of typical BLM (a), SLM (b) and ELM (c) (Khani et al., 2015)

1.3.1 Bulk Liquid Membrane

A BLM system is the simplest form of liquid membrane processes. Generally, F phase and S phase of BLM is separated by a solid impermeable barrier. An organic

membrane phase containing a diluent loaded with carrier placed at the bottom or the top of the aqueous phase according to the density difference between the organic and aqueous phase. The solute will transfer from F phase into S phase with the help of carrier loaded in M phase (Ramkumar & Chanhramouleeswaran, 2015).

1.3.2 Supported Liquid Membrane

The M phase of SLM is usually immobilized in the pores of a microporous hydrophobic solid support. A microporous polymer is used as a support to the liquid membrane and an organic layer can be the micro-porous support. In general, SLM is mainly applicable to polar compounds such as organic acids or bases, charged compounds, and metal ions. According to the report, SLM is a highly sophisticated energy saving process (Mahdavi et al., 2016). There are two major types of SLM: flat sheet supported liquid membrane and hollow fiber supported liquid membrane.

1.3.3 Emulsion Liquid Membrane

Emulsion liquid membrane (ELM) processes can be either designed as water-in-oil emulsion (organic phase as M phase) or oil-in-water emulsion (aqueous phase as M phase). ELM consists of water-in-oil emulsions (or oil-in-water emulsions) which formed by droplets of S phase contained in M phase are suspended in the F phase. The system can provide a high mass transfer rate due to the large surface area within the internal droplets and emulsion globules. The three phases of ELM system are internal phase, membrane phase and external phase. By shearing two immiscible liquids,

emulsions are produced which will provide the energy to reach metastable state by one phase fragment into another (Bhatti et al., 2016)

1.4 Problem Statement

1.4.1 Rhodamine B

Dyes are generally non-biodegradable since the characteristics of high molecular weight and complex chemical structures (Inyinbor et al., 2016). RB is a high water-soluble industrial synthetic dye which is widely used as fluorescent labeling and food coloring due to its low cost, stability and fastness. Further, RB is also used as a systemic marker in a variety of animals and water fluorescent tracer for wildlife studies (Mancuso et al., 2016). The overuse of RB as additive in foodstuffs is harmful to human health. According to the international agency for research on cancer, RB has potential toxic and carcinogenic effects and it also irritates the skin and eyes. However, there are some reports indicate RB has been added to chili powder as a colorant (Zhai et al., 2017 and Long et al., 2016).

1.4.2 Conventional Organic Solvents and Extractants

Organic solvents are the liquids used in liquid membrane system to separate the solute from feeding phase and stripping phase. According to the previous studies, there are some conventional organic solvents used in the liquid membrane process such as cyclohexane (Bohloul et al., 2016), nitrobenzene (Wang et al., 2016), kerosene (Othman et al., 2011), hexane and heptane (Däss & Hamdaoui, 2010). These chemicals,

including the extractant used in like aliquat 336 (Bahloul et al., 2016), di (2-ethylhexyl) phosphoric acid (Hajarabeevia et al., 2008) and mono-(2-etylhexyl) phosphoric acid (Mahdavi et al., 2016), are hazard to the aquatic system and solvent loss in the operation is also considered a potential threat. Therefore, to find an environmental friendly organic solvent become the new objective. The use of vegetable oils as the organic solvent is the achievement of this goal.

1.5 Objectives of Research

The objectives of this research are:

a) To select a suitable vegetable oil-based organic solvent for dye extraction;
b) To optimize the factors (pH, shaking time, shaking speed and ratio of organic to aqueous phase) affecting RB extraction using vegetable-oil-based organic solvent;
c) To select a stripping agent for RB stripping from vegetable oil-based organic solvent;
d) To investigate the effect of viscosity on extraction of RB.

1.6 Thesis Organization

This thesis comprises of 5 chapters:

Chapter 1 (Introduction) gives an introduction of industrial dye wastewater and various types of treatment techniques for dye wastewater. The problem of statement and objectives are also presented in this chapter.

Chapter 2 (Literature Review) includes the overview of the characteristics of Rhodamine B, working principle, transport mechanism and different types of liquid membrane, composition and global consumption of vegetable oils, viscosity and the response surface methodology (RSM).

Chapter 3 (Materials and Methods) presents the chemical agents, equipment used in this research. The experimental procedures of liquid-liquid extraction (LLE) and stripping process, selection of vegetable oil a suitable stripping agent, bulk liquid membrane (BLM) system. There is also a schematic flow diagram to show the overall experimental activities in this chapter.

Chapter 4 (Results and Discussion) includes all the results obtained from this research. The value of viscosities, effect of different factors (pH, O/A ratio, shaking time and shaking speed), the results from LLE system, screening and optimization of factors, stripping efficiency and the results of BLM system.

Chapter 5 (Conclusion and Recommendation) concludes the findings through this research. The findings reflect the objectives which are presented in Chapter 1. The recommendations are also provided for future study.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This chapter aimed to introduce the characteristics of RB, followed by an overview of liquid membrane including the working principles, transport mechanism and three different types of liquid membrane. Vegetable oils as the organic solvents used in this research are also presented by their global consumption, the fatty acids composition and viscosities. Lastly, the response surface methodology (RSM) is reviewed as the statistical optimization technique.

2.1 Classification of Dyes

There are two types of textile dyes: natural dyes and synthetic dyes. Few of natural dyes are carcinogenic since the sources of natural dyes are plants, nuts, tree barks and so on. Generally, the dyes used in the textile industry are basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes and sulfur dyes, where azo derivatives are the major class of dyes that are used in the industry today (Mohamad et al., 2011). Dyes can be classified according to their performance in the dyeing process, which are cationic, anionic and nonionic dyes. Cationic dyes are basic dyes while the anionic dyes include direct, acid and reactive dyes (Seow & Lim, 2016). Table 2.1 presents the typical dyes used in textile dyeing industries.

Table 2.1 Dyes used in textile dyeing operations (Seow & Lim, 2016)

Dye Classification	Description
Basic	Water-soluble, applied in weakly acidic dyebaths
Acid	Water-soluble anionic compounds
Direct	Water-soluble, anionic compounds; can be applied directly to cellulosics without mordants (or metals like chromium and copper)
Reactive	Water-soluble, anionic compounds; largest dye class
Disperse	Water-insoluble
Sulfur	Organic compounds containing sulfur or sodium sulfide
Vat	Water-insoluble; oldest dyes; more chemically complex

2.2 Characteristics of Rhodamine B

Reactive dyes chemically reacted with the fibers with the formation of covalent bond between the dye and the fiber. RB is under the group of reactive dyes and its molecular formula of RB is $C_{28}H_{31}ClN_2O_3$ with the molecular weight of 479.02 gm/mol. The chemical structure of RB is shown as Figure 2.1 (Al-Kadhemy et al., 2011). There are several treatment techniques for RB such as adsorption (Jiang & Huang, 2016), photocatalytic degradation (Pascariu et al., 2016), liquid-liquid extraction (Muthuraman & Teng, 2009), coagulation, and flocculation (Nidheesh & Gandhimathi, 2014; Shakir et al., 2009).

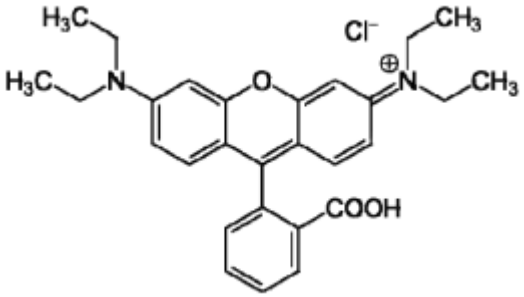

Figure 2.1 Chemical structure of rhodamine B (Muthuraman & Teng, 2009)

2.3 Liquid-Liquid Extraction

Extraction is the pulling or drawing out of something from something else. Chemists extract the compounds from liquids or solids using aqueous or organic solvents. Liquid-liquid extraction (LLE) is a process that can be easily implemented in industry. It is based on the principle of a solute can distribute itself in a certain ratio between immiscible, or partially miscible solvents, and the extraction process depends on the mass transfer rate (Muthraman & Soniya, 2015). LLE is the most effective method to enrich metal ions (Panigrahi et al., 2016). The removal of synthetic dye by using LLE process are also investigated (El-Ashtoukhy & Fouad, 2015), (Modak et al., 2016) and (Chen et al., 2013).

The advantages of LLE including high throughput, selective separation, easy automatic operation and high purification. There are also some drawbacks of LLE: the most of organic solvent required for the process are toxic and the large amounts of organic wastes generated can interfere with the phase separation process (Elumalai et al., 2014; Muthuraman, 2011).

2.4 Transport Mechanism of Liquid Membrane

The working principles of liquid membrane include two homogeneous and miscible liquids, known as feeding phase (F) and stripping phase (S), separated by a third immiscible or partial soluble liquid in the former two liquids which is called the membrane phase (M). In general M phase is organic phase, F phase and S phase are aqueous phase. Figure 2.2 shows a simple equilibrium transport of LM process: solute A is extracted from F phase into M phase, followed by stripping of solute A from the M phase into S phase. Figure 2.3 shows a simple uphill transport of LM process: solute A diffuses from F phase to M phase due to its solubility and bonds irreversibly to reagent B from the S phase, forming compound AB which is insoluble in M phase. When the concentration of AB in S phase is greater than the concentration of solute A in the F phase, solute A is transported from F phase to S phase (liquid membrane). When M phase contains a carrier will complex with solute A, there are two different processes at two phases. At the interphase of F/M, solute A-carrier complex is formed and carrier is broken down at the interphase of M/S. This is called carrier facilitated transport. (Figure 2.4). If an equivalent amount of some component is co-transferred from S phase to the F phases during the transport of solute A from F phase to S phase, then it is known as carrier facilitated coupled transfer. (Figure 2.5) (Jayshree, 2015).

The facilitated transport mechanism could generally achieve a higher selectivity to separate solutes with small amount of extractant added to the M phase. The simple transport mechanism, which depends on the solubility and diffusion coefficients of solutes in M phase, will provide a lower selectivity. Therefore, the facilitated transport

mechanism is widely used in virous liquid membrane process (Muthuraman et al., 2009; He et al., 2000; Tarditi et al., 2008).

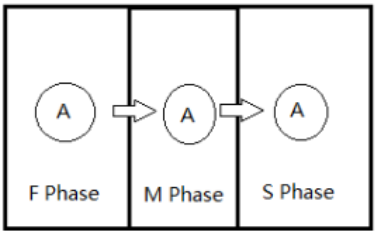

Figure 2.2 Simple equilibrium transport (Jayshree, 2015)

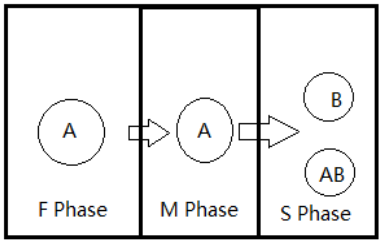

Figure 2.3 Simple uphill transport (Jayshree, 2015)

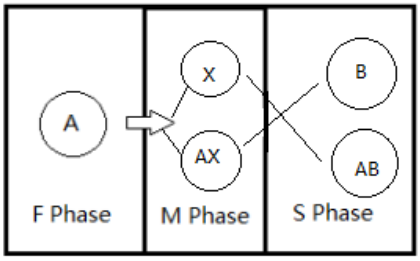

Figure 2.4 Carrier facilitated transfer (Jayshree, 2015)

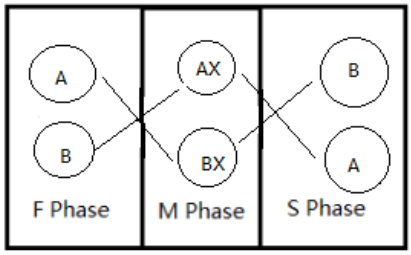

Figure 2.5 Carrier facilitated coupled transfer (Jayshree, 2015)

2.5 Bulk Liquid Membrane

BLM is the simplest type of non-dispersive liquid membrane and it is effective to study the parameters of a system affecting component transfer across the membrane. Generally, BLM consists of aqueous feeding and receiving phases separated by a bulk organic, water-immiscible liquid phase. The phases may be separating by flat vertical walls which separate the feeding and receiving phases from the LM or module configuration may be without flat vertical walls (layered BLM) (Vladimir 2010). Figure 2.6 and Figure 2.7 present BLM with flat vertical wall (Han et al., 2017; Yang

& Feng, 1999; Chakrabarty et al., 2009) and BLM without any separating wall (Muthuraman & Teng, 2009b; León & Guzmán 2004; Yaftian & Burgard, 2006) were used by numerous researchers in virous separation process. In any of these cases, membrane phase is always in contact with feeding phase and receiving phase.

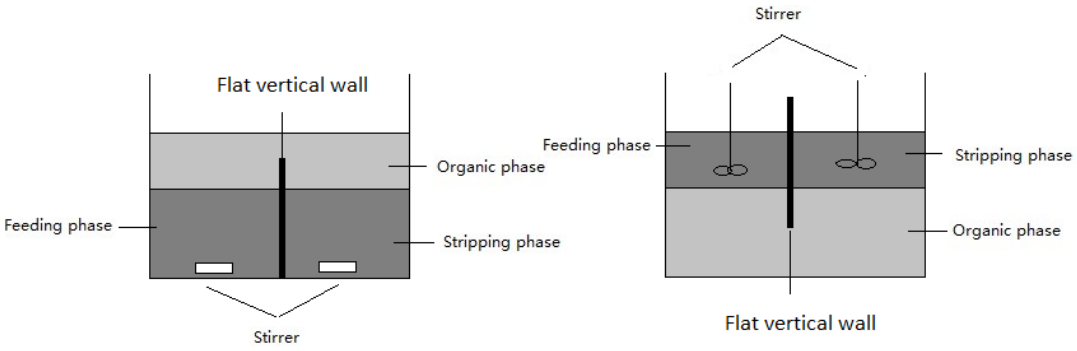

Figure 2.6 BLM with flat vertical wall (Han et al., 2017; Yang & Feng, 1999; Chakrabarty et al., 2009)

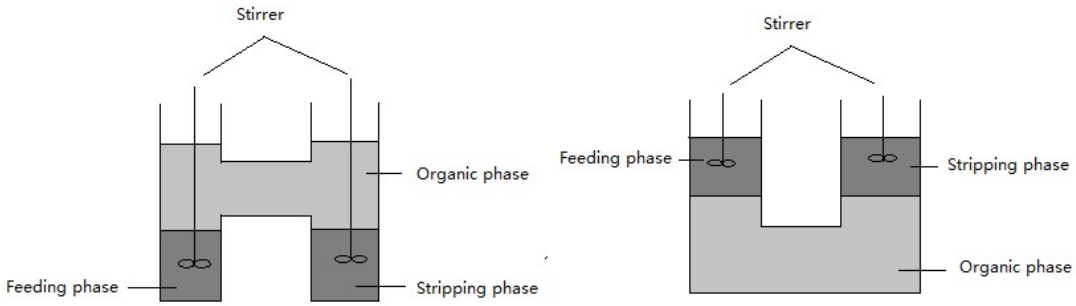

Figure 2.7 BLM without flat vertical wall (Muthuraman & Teng, 2009b; León & Guzmán 2004; Yaftian & Burgard, 2006)

2.6 Factors Affect Rhodamine B Extraction

There are many factors will affect the extraction of dye molecules such as pH of feeding phase, initial dye concentration, concentration of extractant, ratio of organic

to aqueous phase, mixing speed, mixing time viscosity of membrane phase and temperature. In-depth study and optimization of these parameters will greatly help in the development of industrial-scale treatment process for the dye removal. According to the reports by several researchers, the factors of pH of feeding phase, concentration of extractant ratio of F/M phase and initial dye concentration are considered as significant affecting solute transfer during the LM process (Han et al., 2017; Schlosser et al., 2001; Nisola et al., 2010). The viscosity of membrane phase, mixing speed and temperature only affect the transfer rate of solute (Chang et al., 2011; Bassane et al., 2016; Muthuraman & Teng, 2009b).

2.7 Distribution Coefficient

In a typical LLE system, solute might not completely transfer into the organic layer and also partially dissolve in the aqueous layer at the same time. For water-soluble organic materials, most of the solutes will reside in the water phase. A quantitative measurement of how an organic compound distributed between aqueous and organic phase is called the distribution or partition coefficient (Söderlund et al., 2013).

The Distribution Ratio (*D*) will be calculated according to:

$$D = \frac{[Dye]_{org}}{[Dye]_{aq}} = \frac{[Dye]_{ini} - [Dye]_{aq}}{[Dye]_{aq}}$$

(Eq. 2. 1)

where $[Dye]_{ini}$: initial dye concentration in the aqueous phase; $[Dye]_{aq}$: dye concentration of aqueous phase after extraction;$[Dye]org$: dye concentration in the organic phase

In this research, high value of *D* refers to large amount of RB reside in organic phase and a low concentration in the feeding phase, whereas low values of *D* present a high concentration of RB in feeding phase which indicate the transfer of RB is weak.

2.8 Vegetable Oils

Vegetable oils are the lipid materials extracted from beans, seeds (such as soybean oil, corn oil, sunflower oil, etc.) or assortment of fruits (olive oil, palm oil, etc.). They are mostly used for cooking, and in various kinds of foods and snacks. Vegetable oils are environmental friendly considered of their characteristics of biodegradable, non-toxic and renewable (Orsavova et al., 2015).

The demand of vegetable oils is continuously increasing in the past decades and the statistic shows the global consumption of vegetable oil from 1995/1996 to 2015/2016 (Figure 2.8 related with Appendix A). In the year of 2015, more than 150 tons of vegetable oils are consumed all over the world. Among all vegetable oils, the consumption of palm oil is the highest during the past decade. The total consumption value of palm oil, soybean oil, canola oil and sunflower oil accounted for more than 80% of worldwide consumption (Statista, 2016).

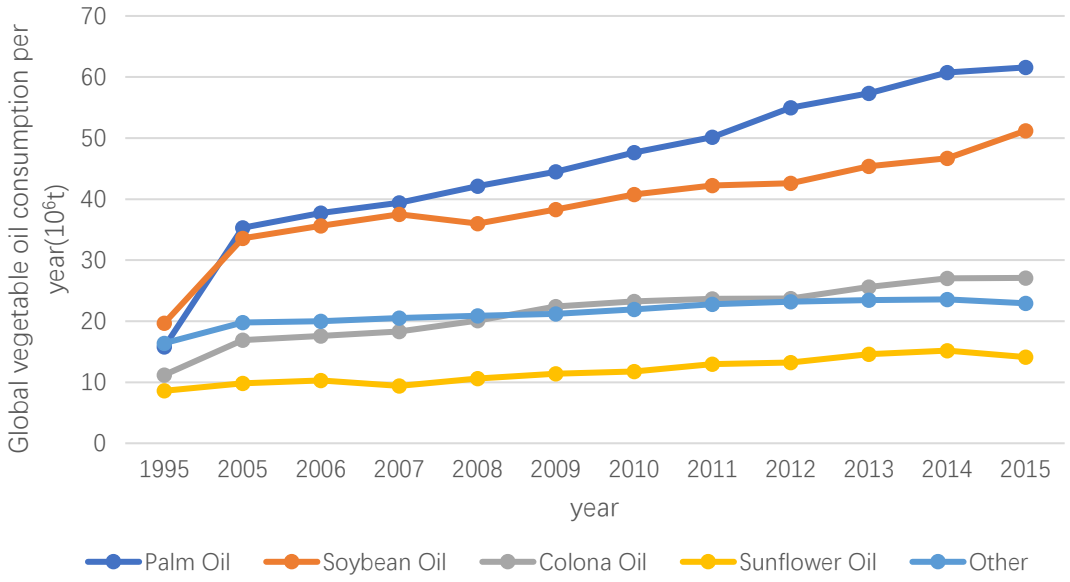

Figure 2. 8 Global consumption of vegetable oils 1995/1996 to 2015/2016 (Statista, 2016)

2.8.1 Composition of Vegetable Oils

On vegetable oils, every position of the glycerol molecule may be esterified by different fatty acids. The most common forms of triacylglycerols (TAG) are present in the molecule of two or three kinds of fatty acids. Generally, the different kind and proportion of triacylglycerols of fatty acids have a great influence on both physical and chemical characteristics of oils and fats. The fatty acids can be classified as saturated fatty acids (SFAs, without double bonds), monounsaturated fatty acids (MUFAs, with one double bond) and polyunsaturated fatty acids (PUFAs, with two to six double bonds). Fatty acids composition of vegetable oils is the mixture of saturated and monounsaturated fatty acids or mixture of saturated and polyunsaturated fatty acids (Orsavova et al., 2015). Table 2.2 shows the fatty acid composition of soybean, corn, canola and sunflower oil (Soon Soon Oil Mill Sdn. Bhd., Malaysia).