SIMULTANEOUS EXTRACTION AND STRIPPING OF Cu(II) IONS THROUGH VEGETABLE OIL-BASED BULK LIQUID MEMBRANE

by

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		Unit
A	Pre-exponential/frequency factor	-
A	Valence of metal species	-
B	Number of di-2-ethylhexylphosphoric acid (D2EHPA) molecules engaged in reaction	-
C_{Fo}	Initial solute concentration in feed phase	mg/L
C_F	Instantaneous solute concentration in feed phase	mg/L
C_M	Instantaneous solute concentration in membrane phase	mg/L
C_S	Instantaneous solute concentration in stripping phase	mg/L
Cd(II)	Cadmium(II) ion	-
$\mathrm{CH_3COOH}$	Acetic acid	-
$\mathrm{CH_3COONa}$	Sodium acetate	-
Cr(VI)	Chromium(IV) ion	-
Cu(II)	Copper(II) or Cupric ion	-
$[\mathrm{Cu}]_{\mathrm{o,F}}$	Initial Cu(II) ion concentration in feed phase	mg/L, mM
$[\mathrm{Cu}]_{\mathrm{f,F}}$	Final Cu(II) ion concentration in feed phase	mg/L
$[\mathrm{Cu}]_{\mathrm{f,S}}$	Final Cu(II) ion concentration in stripping phase	mg/L
$[\mathrm{Cu}]_{\mathrm{f,org,ext}}$	Final Cu(II) ion concentration in organic phase after extraction	mg/L, mM
$[\mathrm{Cu}]_{\mathrm{f,org,str}}$	Final Cu(II) ion concentration in organic phase after stripping	mg/L
Cu-D2EHPA	Cu-D2EHPA complex	-
[Cu-D2EPHA]	Concentration of D2EHPA that is associated with Cu(II) ion in organic phase	mM
$\mathrm{CuSO_4.5H_2O}$	Copper sulphate pentahydrate	-
D	Number of fitted parameters	-
D	Distribution ratio	-
[D2EHPA]	Concentration of D2EHPA	mM
E_a	Activation energy	kJ/mol
[free-D2EHPA]	Concentration of D2EHPA that is not associated	mM

	with Cu(II) ion in organic phase	
F-test	Fisher's test	-
H^+	Proton	-
HCl	Hydrochloric acid	-
Hg(II)	Mercury(II) ion	-
HNO_3	Nitric acid	-
$(HR)_2$	Dimeric form of D2EHPA	-
H_2SO_4	Sulphuric acid	-
$[H_2SO_4]$	Concentration of sulphuric acid	M
J_F	Instantaneous solute flux in feed phase	h^{-1}
J_F^{max}	Maximum solute flux in feed phase	h^{-1}
J_M	Instantaneous solute flux in membrane phase	h^{-1}
J_S	Instantaneous solute flux in stripping phase	h^{-1}
J_S^{max}	Maximum solute flux in stripping phase	h^{-1}
K	Number of factors studied	-
k_1	Rate constant of extraction process	h^{-1}
k_2	Rate constant of stripping process	h^{-1}
k_{2M}	k_2 derived from Eq. (2.10)	h^{-1}
k_{2S}	k_2 derived from Eq. (2.11)	h^{-1}
K_a	Dissociation constant	-
K_d	Distribution constant	-
K_{di}	Dimerization constant	-
K_{ex}	Equilibrium constant of extraction reaction	-
K_{sp}	Solubility product constant	-
L	Metal species	-
$LR_2(HR)_b$	Metal-D2EHPA complex	-
Mn(II)	Manganese(II) ion	-
N	Number of data points	-
N	Number of replicate samples	-
NaOH	Sodium hydroxide	-
Na_2SO_4	Sodium sulphate	-
$[Na_2SO_4]$	Concentration of sodium sulphate	mM
O:A	Organic to aqueous phase ratio	-

OH^-	Hydroxide anion	-
P	Probability	-
P_{vap}	Vapour pressure	kPa
P	Fraction size of a full factorial design	-
Pb(II)	Lead(II) ion	-
P=O	Phosphoryl functional group	-
pH_{eq}	Equilibrium pH	-
$pH_{f,F}$	Final pH of the feed phase	-
$pH_{o,F}$	Initial pH of the feed phase	-
R	Universal gas constant	8.314 J/mol·K
R^2	Coefficient of determination	-
$R^2(adj)$	Adjusted R^2	-
R_F	Reduced solute concentration in feed phase	-
R_M	Reduced solute concentration in membrane phase	-
R_M^{max}	R_M at which maximum fluxes are reached	-
R_S	Reduced solute concentration in stripping phase	-
SD_{coef}	Standard deviation of coefficient	-
SD_{reg}	Standard deviation of regression	-
S:F	Stripping/membrane to feed/membrane interface area ratio	-
T	Absolute temperature	K
T_f	Flash point	K
T_m	Melting point	K
t	Time elapsed	H
t_{max}	Time at which maximum fluxes are reached	H
t_{mix}	Mixing time	Min
t_{set}	Settling time	Min
[TBP]	Concentration of tributylphosphate	mM
Th(IV)	Thorium(IV) ion	-
t-stat	*t*-statistics	-
$\bar{x}$	Mean of replicate samples	%
x_i	Independent variable in coded unit	-
X_i	Independent variable in uncoded unit	-

X_{high}	High value of independent variable	-
X_{low}	Low value of independent variable	-
y	Dependent variable	-
Zn(II)	Zinc(II) ion	-
$\Delta G°$	Change in standard free energy	kJ/mol
$\Delta H°$	Change in standard enthalpy	kJ/mol
$\Delta S°$	Change in standard entropy	kJ/mol

Greek Letters

α	Distance between the star and centre points in central composite design	-
β_i	Regression coefficient of linear term	-
β_{ii}	Regression coefficient of quadratic term	-
β_{ij}	Regression coefficient of interaction term	-
β_o	Regression coefficient of intercept term	-
δ	Hildebrand solubility parameter	$(MPa)^{1/2}$
ε	Error term	-
μ	Viscosity	mPa.s

LIST OF ABBREVIATION

AAS	Atomic absorption spectrophotometer
ANOVA	Analysis of variance
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared
BLM	Bulk liquid membrane
CCD	Central composite design
CI	Confidence interval
D2EHPA	Di-2-ethylhexylphosphoric acid
DF	Degrees of freedom
ELM	Emulsion liquid membrane
EU	European Union
F	Feed
FAAS	Flame atomic absorption spectrophotometer
FTIR	Fourier transform infrared
LLE	Liquid-liquid extraction
M	Membrane
MS	Mean square
RSD	Relative standard deviations
RSM	Response Surface Methodology
S	Stripping
SD	Standard deviation
SER	Standard error of residuals
SG	Specific gravity
SLM	Supported liquid membrane
SS	Sum of squares
SSE	Error sum of squares
SST	Total sum of squares
TBP	Tributylphosphate
TLV	Threshold limit value
TLV-C	TLV-ceiling limit
TLV-STEL	TLV-short term exposure limit
TLV-TWA	TLV-time weighted average
USA	United States of America

PENGEKSTRAKAN DAN PENGEMBALIAN SERENTAK ION Cu(II) DENGAN MENGGUNAKAN MEMBRAN CECAIR PUKAL BERASASKAN MINYAK TUMBUHAN

ABSTRAK

Penyelidikan ini bertujuan untuk menyiasat kebolehlaksanaan untuk menggantikan pelarut organik berasaskan petroleum, yang tidak dapat diperbaharui dan selalu beracun, dengan pelarut organik berasaskan minyak tumbuhan, yang lebih dapat diperbaharui dan mesra alam, sebagai fasa membran sebuah membran cecair pukal (BLM) untuk menyingkir dan mengembalikan ion Cu(II) dari larutan akueus dalam satu unit. Keputusan daripada pengekstrakan pelarut eksperimen menunjukkan bahawa pelarut organik berasaskan minyak kacang soya (minyak kacang soya yang mengandungi asid di-2-etilheksilfosforik (D2EHPA) (pengekstrak (pembawa)) dan tributilfosfat (TBP) (pengubah fasa)) dan 1.5 M asid sulfurik (H_2SO_4) adalah pelarut organik dan agen pengembalian yang paling sesuai untuk menyingkir dan mengembalikan ion Cu(II). Dengan menggunakan Kaedah Permukaan Reaksi (RSM), keadaan optimum untuk mencapai pengekstrakan maksimum ion Cu(II) ditentukan seperti yang berikut: 85.43 mM kepekatan D2EHPA ([D2EHPA]), 4.47 pH keseimbangan, 3 minit masa mencampur, 1 nisbah fasa organik kepada akueus, 200 mM kepekatan natrium sulfat dan 30 mM kepekatan TBP. Stoikiometri (4:1 nisbah stoikiometri D2EHPA kepada ion Cu(II)) dan struktur (sfera dalaman) Cu-D2EHPA kompleks (spesis ekstrak), serta muatan kapasiti (2400 mg/L (37.82 mM) ion Cu(II)) dan kitar semula (sebanyak 10 pengekstrakan-pengembalian kitar) pelarut organik berasaskan minyak kacang soya juga dikaji. Parameter reka bentuk (pengacauan semua fasa dan 2.5:1 nisbah luas antara muka pengembalian/membran kepada suapan/membran) yang paling sesuai untuk sebuah BLM berasaskan minyak kacang soya dipilih dan parameter operasinya yang optimum untuk mencapai pengembalian maksimum ion Cu(II) ditentukan dengan menggunakan RSM seperti yang berikut: 87.43 mM [D2EHPA], 150 rpm kelajuan kacauan, 313 K suhu, 24 jam masa operasi dan 1.5 M kepekatan asid sulfurik ([H_2SO_4]). Langkah penghadan kadar untuk process pengekstrakan (kawalan pembauran) dan pengembalian (kawalan tindak balas kimia) untuk BLM berasaskan minyak kacang soya ditentukan dan satu mekanisme pengangkutan berganding pembilang pemudahan dicadangkan. Perbandingan pemalar kadar pengekstrakan (k_1) dan pengembalian (k_2) di antara BLM berasaskan minyak kacang soya dan minyak parafin menunjukkan nilai pemalar untuk kedua-dua sistem adalah lebih kurang sama (BLM berasaskan minyak kacang soya: k_1 = 1.94 jam^{-1}, k_2 = 0.11 jam^{-1}; BLM berasaskan minyak parafin: k_1 = 1.73 jam^{-1}, k_2 = 0.13 jam^{-1}). Kinetik angkutan bagi ion Cu(II) melalui BLM berasaskan minyak kacang soya didapati tidak dipengaruhi oleh pelbagai ion bukan organik yang terdapat di dalam air buangan industri.

SIMULTANEOUS EXTRACTION AND STRIPPING OF Cu(II) IONS THROUGH VEGETABLE OIL-BASED BULK LIQUID MEMBRANE

ABSTRACT

This research aims to examine the feasibility of replacing the classical petroleum-based organic solvents, which are non-renewable and invariably toxic, with the vegetable oil-based ones, that are more renewable and environmentally benign, as the membrane phase of a bulk liquid membrane (BLM) for simultaneous extraction (removal) and stripping (recovery) of Cu(II) ions in a single unit. The liquid-liquid extraction results revealed that soybean oil-based organic solvent (soybean oil loaded with di-2-ethylhexylphosphoric acid (D2EHPA) (extractant (carrier)) and tributylphosphate (TBP) (phase modifier)) and sulphuric acid (H_2SO_4) of 1.5 M were the most suitable organic solvent and efficient stripping agent, respectively, for Cu(II) ion extraction and stripping. By means of Response Surface Methodology (RSM), the optimum conditions for maximum Cu(II) ion extraction were determined as follows: D2EHPA concentration ([D2EHPA]) of 85.43 mM, equilibrium pH of 4.47, mixing time of 3 min, organic to aqueous phase ratio of 1, sodium sulphate (inert salt) concentration of 200 mM, and TBP concentration of 30 mM. The stoichiometry (stoichiometric ratio of D2EHPA to Cu(II) ion of 4:1) and structure (inner sphere) of Cu-D2EHPA complexes (extracted species), as well as the loading capacity (2400 mg/L (37.82 mM) of Cu(II) ions) and reusability (up to 10 consecutive extraction-stripping cycles) of soybean oil-based organic solvent were also investigated. The suitable design parameters (stirring of all phases and stripping/membrane to feed/membrane interface area ratio of 2.5:1) for a soybean oil-based BLM were selected and its operating parameters ([D2EHPA], H_2SO_4

concentration ([H_2SO_4]), stirring speed, temperature and operating time) were optimised for maximum Cu(II) ion stripping by RSM as follows: [D2EHPA] of 87.43 mM, stirring speed of 150 rpm, temperature of 313 K, operating time of 24 h, and [H_2SO_4] of 1.5 M. The rate-controlling steps of both extraction (diffusion-controlled) and stripping (chemical reaction-controlled) processes in soybean oil-based BLM were determined and a facilitated counter coupled-transport mechanism was proposed. A comparison of the extraction (k_1) and stripping (k_2) rate constants between the soybean oil- and kerosene-based BLMs revealed that they were quite compatible with each other (soybean oil-based BLM: k_1 = 1.94 h^{-1}, k_2 = 0.11 h^{-1}; kerosene-based BLM: k_1 = 1.73 h^{-1}, k_2 = 0.13 h^{-1}). The transport kinetics of Cu(II) ions through soybean oil-based BLM was found not to be affected by various inorganic ions present in the real industrial wastewater.

CHAPTER 1

INTRODUCTION

1.0 Research Overview

This chapter gives an overview of the research background. It covers the current scenario of heavy metal pollution in water and various treatment techniques used for metal-containing wastewater. The needs to develop greener and more cost-effective treatment techniques for Cu(II) ion-containing wastewater are highlighted. The objectives and organization of thesis are also presented.

1.1 Industrial Wastewater – Source of Heavy Metal Pollution

Water plays a vital role in sustaining livelihoods and driving all socio-economic development. With the rapidly increasing industrialization and urbanization, waterways are contaminated with heavy metals by means of various industrial activities such as mining, batteries, fertilizers, pesticide, textiles, petroleum refineries, electrical and electronic, electroplating, metal processing and finishing (Nemerow and Agardy, 1998; Nemerow, 2007). This poses a serious threat to the environment owing to the toxicity, bio-accumulation tendency, and persistency in nature of the heavy metals discharged (Csuros and Csuros, 2002). Various detrimental impacts of heavy metals on human health (Esminger and Esminger, 1994; Agarwal, 2009) and other living organisms like fish (Amanulla-Hameed et al., 2006; Oliva et al., 2009; Palaniappan and Karthikeyan, 2009) and seaweeds (Sasikumar and Subramaniyan, 2006) are well-documented in the literatures. In Malaysia, industrial wastewater containing heavy metals is classified as scheduled waste under the Environmental Quality (Scheduled Wastes) Regulations 1989 (EQA,

2010) and, hence, must be properly treated prior to discharge. The maximum permissible discharge limits of various heavy metals are generally below 5 mg/L, for instance 0.2 and 1 mg/L for copper under Standards A and B (Table A.1 in Appendix A), respectively, as stipulated by Environmental Quality (Sewage and Industrial Effluents) Regulations 2009 (EQA, 2010).

1.2 Treatment Techniques for Metal-Containing Wastewater

Wastewater treatment techniques can be broadly classified into two categories, namely physicochemical and biological techniques. The former is based on either physical separation or chemical reaction, while the latter makes use of biological materials, for instance activated sludge (Kılıç et al., 2008), bacteria (Hsu et al., 2010), plants (Davis et al., 2003), agricultural (Aksu and İşoğlu, 2005) and food (Kawasaki et al., 2010) wastes, to remove pollutants from wastewater. Selection of treatment techniques for a specific type of wastewater is normally based on the fundamental properties of pollutants and experience. Since heavy metals are non-biodegradable, the physicochemical techniques are more appropriate to treat metal-containing wastewater as compared with the biological ones as mentioned above. The conventional physicochemical techniques used in this instance include chemical precipitation, coagulation-flocculation, clarification, membrane filtration, ion exchange, and adsorption. Nevertheless, these techniques possess their own inherent disadvantages and none of them is universal in treating all kinds of metal-containing wastewater. Table 1.1 summarizes the advantages, disadvantages, efficiencies and the suitable working ranges of metal concentration for some conventional physicochemical treatment techniques. Being conventional treatment techniques which are used widely throughout various industries, all of these techniques have the advantages of being well-established and proven effective in the industries. Other advantages vary from one method to another, but are generally associated to operation simplicity, small space requirement, high efficiency, and low cost. The disadvantages of these techniques, on the other hand, are related to high cost, chemical interference, potential hazard and limited efficiency. On the whole, all of these treatment techniques can achieve removal efficiencies of up to 100% provided that the equipment used is in good condition and the techniques are conducted under appropriate operating conditions. While most of these treatment techniques are suitable for wastewater containing heavy metals of concentration more than 10 mg/L, ion exchange and adsorption, on the contrary, favours that with concentration less than 100 mg/L.

Table 1.1 Advantages, disadvantages, efficiencies and suitable working ranges of metal concentration for some conventional physicochemical treatment techniques

Techniques	Advantages	Disadvantages	Efficiency (%)	Suitable working range of metal concentration (mg/L)	References
Chemical precipitation	■ Well-established and proven effective in industry ■ Simple operation ■ Low energy consumption and, thus, low operating cost ■ Low capital cost ■ Not metal selective	■ Susceptible to chemical interference in the treatment of mixed wastes ■ Production of substantial quantity of sludge ■ Extra operating cost for sludge disposal ■ Not metal selective	> 80	> 10	Noyes, 1993; Aderhold et al., 1996; Eccles, 1999; Charerntanyarak, 1999; Wang et al., 2005; Kurniawan et al., 2006a; Pang et al., 2009
Coagulation-flocculation	■ Well-established and proven effective in industry ■ Good sludge settling	■ Production of substantial quantity of sludge ■ Extra operating cost for sludge disposal ■ Highly pH-dependent processes ■ Applications of alum and polyacrylamide (which may contain unpolymerized acrylamide) pose a potential hazard	> 90	> 10	Charerntanyarak, 1999; Shammas, 2005; Kurniawan et al., 2006a; O’Conell et al., 2008; Renault et al., 2009; Pang et al., 2009

Table 1.1 Continued

Techniques	Advantages	Disadvantages	Efficiency (%)	Suitable working range of metal concentration (mg/L)	References
Clarification	▪ Well-established and proven effective in industry ▪ Good sludge settling, particularly for slow-settling suspended matters ▪ Shorter retention time and more compact system than the simple sedimentation systems	▪ Higher capital, operating and maintenance costs than the simple sedimentation systems	> 80	> 10	Noyes, 1993; Edzwald et al., 1998; Wang et al., 2005; O'Conell et al., 2008; Cushnie, 2009
Membrane filtration	▪ Well-established and proven effective in industry ▪ Compact system	▪ Susceptible to membrane fouling, scaling and degradation ▪ High capital and maintenance costs ▪ High operating cost	> 90	> 10	Noyes, 1993; Eccles, 1999; Kurniawan et al., 2006a; Divrikli et al., 2007
Ion exchange	▪ Well-established and proven effective in industry ▪ Compact system ▪ Metal selective ▪ High metal recovery ▪ No sludge generation	▪ Susceptible to resin fouling and degradation	> 95	< 100	Noyes, 1993; Eccles, 1999; Kurniawan et al., 2006a; Misra et al., 2011
Adsorption	▪ Well-established and proven effective in industry ▪ High metal removal ▪ Possible for selective adsorption ▪ No sludge generation	▪ Conventional activated carbons are relatively expensive	> 95	< 100	Eccles, 1999; Ekinci et al., 2002; Kurniawan et al., 2006a; Kurniawan et al., 2006b

1.3 Problem Statements

Wastewater containing a substantial amount of Cu(II) ions poses a health threat to living things but could serve as a good source for Cu(II) ion recovery if it is treated efficiently (Agrawal and Sahu, 2010). The recovered Cu(II) ions can be either recycled back to the process lines for reuse or reduced to its metal form by electrowining processes (Komulainen et al., 2009). Although most of the wastewater treatment techniques could achieve a fairly high removal efficiency of heavy metals (Table 1.1), there is little emphasis on the recovery of the removed metals which, if available, is normally carried out in a separate unit by elution with suitable reagents and this incurs additional cost (Kurniawan et al., 2006a). Recently, a technique that extracts (removes) and strips (recovers) heavy metals in a single unit, namely liquid membrane, has been given a considerable attention by many researchers (Singh et al., 2011; Kandwal et al., 2012) due to its pronounced advantages such as simultaneous extraction and stripping of heavy metals in a single unit, uphill trasnport, high selectivity, high recovery, and low energy consumption (Gu, 2003; Ren et al., 2008). However, the conventional organic solvents used in liquid membrane are mostly derived from petroleum resources, for instance kerosene- (Kumbasar, 2009b), toluene- (Altin et al., 2010), hexane- (Muthuraman et al., 2009a) and chloroform-based (Reddy et al., 2010) ones, which are invariably toxic and non-biodegradable. Consequently, they are difficult to handle and often result in ecological hazard to the aquatic systems in the case of solvent loss (Watson, 1999). Solvent loss also implies the increase in solvent consumption and, hence, a rise in the material cost since the conventional petroleum-based organic solvents could be inordinately expensive due to the limited resources. To manage the metal-containing wastewater according to the principles of sustainable development, greener solvents such as the vegetable oil-based ones should be used in liquid membrane processes (Venkateswaran et al., 2007).

Although vegetable oil-based organic solvents have been used in supported liquid membrane (SLM) to extract and strip various pollutants, for instance dye (Muthuraman and Palanivelu, 2006), phenol (Venkateswaran and Palanivelu, 2006), rhodamine B (Muthuraman and Teng, 2009a), Cu(II) (Venkateswaran et al., 2007), and Hg(II) (Chakrabarty et al., 2010), from aqueous solutions, there has not been any report of its application in bulk liquid membrane (BLM). While most of the research on BLM focus on the optimization of operating parameters by the univariate technique (Muthuraman et al., 2009a; Chakrabarty et al., 2009), application of the multivariate technique such as Response Surface Methodology (RSM) in this instance has not been reported. Moreover, there is relatively little study on the design and kinetic parameters of BLM which are essential for selecting the optimum design and operating conditions for a full-scale batch process. The rate-controlling steps of transport processes in BLM, which is rarely reported by other researchers, can also be determined from the kinetic parameters obtained.

1.4 Objectives of Research

The objectives of this research are:

(a) To select a suitable vegetable oil-based organic solvent for Cu(II) ion extraction from aqueous solutions and a suitable stripping agent for Cu(II) ion stripping from the loaded vegetable oil-based organic solvent

(b) To optimize the factors affecting Cu(II) ion extraction from aqueous solutions using vegetable oil-based organic solvent

(c) To determine the stoichiometry and structure of Cu(II)-organic complexes (extracted species), as well as the loading capacity and reusability of vegetable oil-based organic solvent for Cu(II) ion extraction from aqueous solutions

(d) To select suitable design parameters, optimize the operating parameters, as well as to determine the transport kinetics and mechanism of Cu(II) ions through vegetable oil-based BLM

1.5 Organization of Thesis

This thesis is comprised of six chapters. Chapter 1 (Introduction) presents an overview of heavy metal pollution by industrial wastewater and various treatment techniques used for metal-containing wastewater. The problem statements of research are discussed and its objectives are highlighted. The overall contents of thesis are summarized in the last section of this chapter.

Chapter 2 (Literature Review) reviews the characteristics of Cu(II) ion-containing wastewater, liquid membrane, and conventional organic solvents for heavy metal separation from aqueous solutions. Vegetable oils as the potential greener replacement for the conventional petroleum-based organic solvents are highlighted. The chemistry and thermodynamics of metal extraction, as well as RSM as a statistical multivariate optimization technique are also reviewed.

Chapter 3 (Materials and Methods) presents the materials, equipment, and software programs used throughout the research. The experimental procedures for the preparation of aqueous and organic phases, as well as the extraction and stripping of Cu(II) ions by both liquid-liquid extraction and liquid membrane are elaborated. A schematic flow diagram of the overall experimental activities is also included.

Chapter 4 (Results and Discussion) presents all the results obtained throughout the research. It covers the findings obtained from optimization, efficiency, stoichiometry, and structural studies of Cu(II) ion extraction with vegetable oil-based organic solvents, Cu(II) ion stripping from loaded vegetable oil-based organic solvents with mineral acids, as well as optimization, kinetic, and mechanism studies of Cu(II) ion transport through vegetable oil-based BLM.

Chapter 5 (Conclusions and Recommendations) concludes all the findings obtained from the current research. The conclusions reflect the achievements of the research objectives as listed in Chapter 1. Finally, plausible recommendations for future study in consideration of their significance associated to the present research are proposed.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This chapter begins with an overview of the characteristics of Cu(II) ion-containing wastewater, followed by a review of liquid membrane which covers topics like working principles, transport mechanisms and kinetics, as well as types and comparison of different liquid membranes. Various types of organic solvents for heavy metal separation from aqueous solutions are then presented by highlighting vegetable oils as the potential greener replacement for the conventional petroleum-based organic solvents. The composition, world production, physical properties, and application of vegetable oils in heavy metal separation from aqueous solutions are also included. Lastly, the chemistry and thermodynamics of metal extraction, as well as Response Surface Methodology (RSM) as a statistical multivariate optimization technique are reviewed.

2.1 Characteristics of Cu(II) Ion-Containing Wastewater

Cu(II) ion-containing wastewater is generated from a wide variety of industries, among which, electroplating, electroless plating, metal finishing, and printed circuit board manufacturing industries, which utilize a large amount of Cu(II) ion-containing process solutions, produce wastewater with a substantial amount of Cu(II) ions. Table 2.1 shows the typical wastewater characteristics of electroplating, electroless plating, metal finishing, and printed circuit board manufacturing industries. In general, the wastewater characteristics vary significantly among these industries, but are usually composed of heavy metals (copper, nickel, iron, chromium, and so forth), non-heavy metals (cyanide, fluoride, sulphate, and phosphate), and suspended solids (sand, dirt, grease, oil, and tar). Of all the industries, the printed circuit board manufacturing industry discharges wastewater with the highest Cu(II) ion concentration (up to 535.7 mg/L). This is followed by the electroplating and metal finishing (up to 272.5 mg/L), as well as the electroless plating industries (up to 47.9 mg/L) (U.S. EPA, 1978; Nemerow and Agardy, 1998; Nemerow, 2007).

Table 2.1 Typical wastewater characteristics of electroplating, electroless plating, metal finishing, and printed circuit board manufacturing industries

Pollutants		Types of Industries			
		Electroplating	Electroless plating	Metal finishing	Printed circuit board manufacturing
Type	Name	Concentration ranges (mg/L)			
Heavy metals	Copper	0.032-272.5	0.002-47.9	0.206-272.5	1.582-535.7
	Nickel	0.019-2954	0.028-46.80	-	0.027-8.44
	Chromium total	0.088-525.9	-	0.088-525.9	0.005-38.52
	Chromium hexavalent	0.005-334.5	-	0.005-334.5	0.004-3.543
	Iron	0.41-1482	-	0.075-263	-
	Zinc	0.112-252	-	0.112-200	-
	Tin	0.06-103.4	-	0.068-103.4	-
	Lead	0.663-25.39	-	-	0.044-9.701
	Cadmium	0.007-21.6	-	-	-
	Silver	-	-	-	0.036-0.202
	Gold	-	-	-	0.007-0.19
	Platinum	-	-	-	-
	Palladium	-	-	-	0.008-0.097
Non-heavy metals	Total cyanide	0.005-150	0.005-12	0.005-126	0.002-5.333
	Amenable cyanide	0.003-130	0.005-1	0.005-101.3	0.005-4.645
	Fluoride	0.022-141.7	0.11-18	0.022-141.7	0.648-680
	Sulphate	0.02-340	0.03-110	0.06-340	0.065-50.6
	Phosphate	0.02-144	0.03-109	0.06-144	0.075-33.8
Solids	Total suspended solids (sand, dirt, grease, oil and tar)	0.1-9970	0.1-39	0.1-4340	1-408.7

Source: U.S. EPA, 1978; Nemerow and Agardy, 1998; Nemerow, 2007

2.2 Liquid Membranes

Liquid membrane is a separation system consisting of a liquid film through which selective mass transfer of ions or molecules occurs via permeation and transport processes. Its efficiency and economic advantages have designated it as the optimal solution for some important problems in science and technology such as precious metal recovery (Fontàs et al., 2006), toxic metals (Alpaydin et al., 2011; Singh et al., 2011), non-metals (Pancharoen et al., 2009), and organic molecules (Muthuraman et al., 2009a; Dâas and Hamdaoui, 2010) removal from wastewater, and so forth. Therefore, liquid membrane remains to be an attractive research area despite some technological challenges which, at present, prevent its large scale industrial applications.

2.2.1 Working Principles of Liquid Membrane

Liquid membrane explores a simple working principle: two homogeneous and completely miscible liquids, known as the feed (F) and stripping (S) phases, are spatially separated by a third liquid, called the membrane (M) phase, which is immiscible and practically insoluble in the former two liquids (Figure 2.1). In most cases, the F and S phases are aqueous solutions, while the M phase is an organic solvent. Owing to the favourable thermodynamic conditions created at the F/M and M/S interfaces, solute A is extracted from F into M phase, followed by the back-extraction (stripping) of solute A from the M phase and its accumulation in the S phase (Figure 2.1) (Boyadzhiev and Lazarova, 1995).

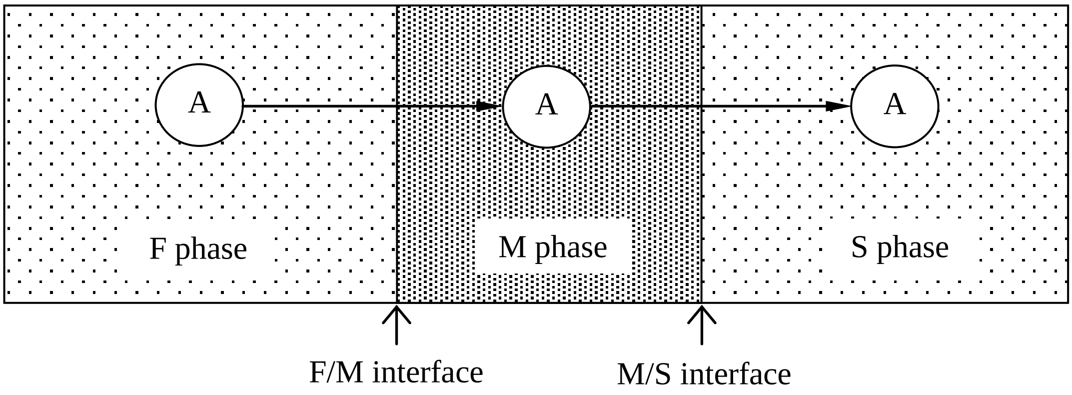


Figure 2.1 Schematic diagram of liquid membrane

2.2.2 Transport Mechanisms of Liquid Membrane

Solutes can be transported through liquid membrane by two mechanisms, namely, simple and facilitated transports (Boyadzhiev and Lazarova, 1995). These mechanisms may be distinguished by the function of M phase during the transport process, in which the former has the M phase acting as a physical solvent for the solutes whereas the latter has it as a liquid substratum containing a selective extractant (carrier) for the solutes.

The simple transport mechanism can be carried out in two ways, namely, simple equilibrium and simple uphill transports. In the simple equilibrium transport, solute A is transferred from F to S phase on account of its solubility in both the M and S phases (Figure 2.2a). This transport process is driven by the concentration gradient of solute A across the M phase and proceeds until the equilibrium condition is reached. In the simple uphill transport, on the other hand, solute A diffuses from F to M phase due to its solubility and bonds irreversibly to a reagent B from the S phase, forming compound AB which is insoluble in the M phase (Figure 2.2b). When the concentration of compound AB in the S phase becomes greater than the concentration of solute A in the F phase, solute A is transported from F to S phase, apparently, counter its concentration gradient and, thus, giving it its name of ‘uphill’ transport.

Unlike the simple transport mechanism, the facilitated transport mechanism does not rely on the solubility of solute A in different phases, but on an active component (extractant) contained in the M phase which reacts selectively and reversibly with solute A by the following scheme:

$$A + X \rightleftarrows AX \tag{2.1}$$

where X is the extractant. In this mechanism, extractant X reacts reversibly with solute A, binding it to form a complex AX at the F/M interface, transporting it through the M phase and releasing it at the M/S interface. This kind of mechanism can be carried out in two different ways: one is by the facilitated uphill transport and the other is by the facilitated coupled transport. In the facilitated uphill transport, the complex AX formed at the F/M interface is destructed at the M/S interface where solute A is bonded irreversibly with a reagent B from the S phase, forming a new compound AB that is insoluble in the M phase. During this process, extractant X is liberated and, due to its own concentration gradient across the M phase, it moves from M/S back to F/M interface where it is free to bind with the next solute A that comes by (Figure 2.2c). In the coupled transport, on the other hand, solute A is coupled to and dependent upon the transport of a reagent B across the M phase. It can be either co-transport or counter-transport, depending on the direction of the coupled fluxes (Chakrabarty et al., 2009). Figure 2.2d shows the facilitated coupled counter-transport of solute A and reagent B across the M phase. In this type of transport, solute A, which is recovered from the F phase and transported by extractant X into the S phase, is substituted by an equivalent amount of reagent B of the same type from the S phase and transported into the F phase.

Between the simple and facilitated transport mechanisms, the latter could generally achieve a higher selectivity to separation of solutes with only a small amount of extractant added to the M phase, while the former, which has to depend on the solubility and diffusion coefficients of solutes in the M phase, provides a lower selectivity to separation (Boyadzhiev and Lazarova, 1995). Therefore, the facilitated transport mechanism, particularly the facilitated counter-coupled transport, is widely applied in various liquid membrane processes to remove and recover heavy metals from aqueous solutions (He et al., 2000; Tarditi et al., 2008; Muthuraman et al., 2009a; Jafari et al., 2009).

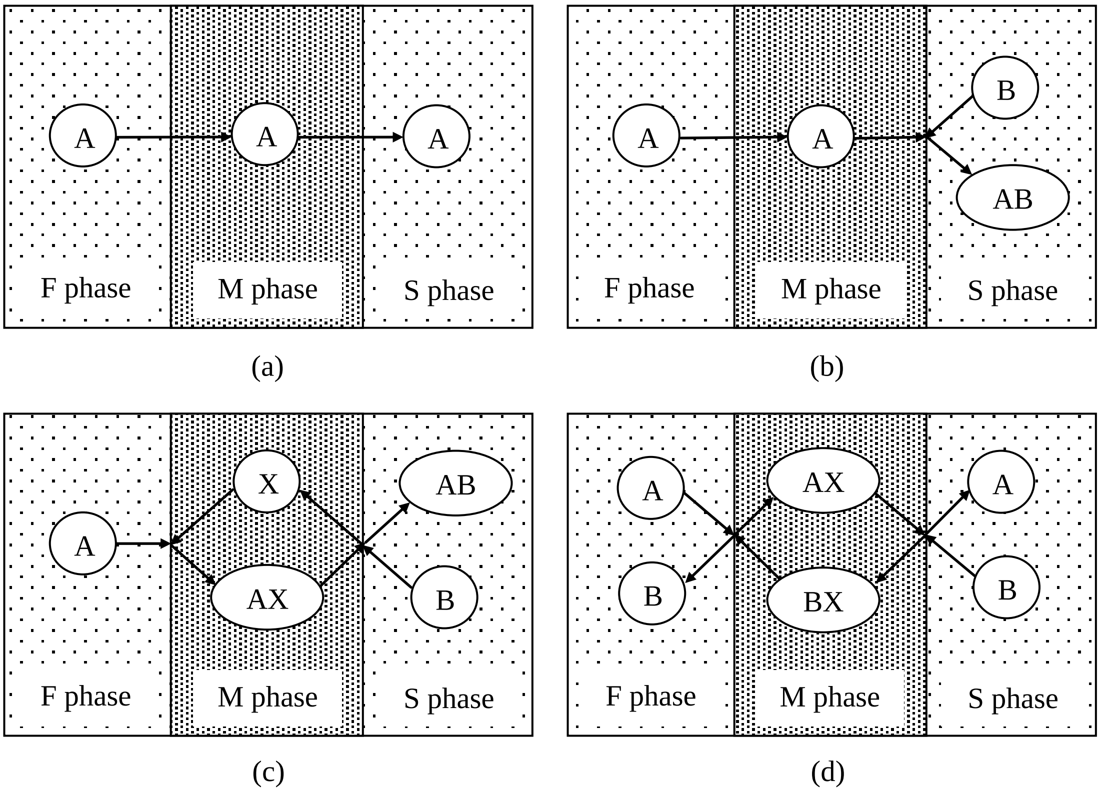


Figure 2.2 Transport mechanisms of liquid membrane: (a) Simple equilibrium transport; (b) Simple uphill transport; (c) Facilitated uphill transport; (d) Facilitated coupled transport

2.2.3 Transport Kinetics of Liquid Membrane

Transport kinetics describes the rate of transporting solutes from one side of a membrane to the other. It controls the rate required to transport solutes across liquid membrane which is essential for selecting the optimum operating conditions for a full-scale batch process. The kinetic parameters are also helpful in determining the rate-controlling steps which are necessary in the design and modelling of liquid membrane processes.

It has been shown by numerous researchers that the facilitated transport of solutes through liquid membrane obeys formally the kinetic laws of two consecutive irreversible first-order reactions according to the kinetic scheme (Szpakowska and Nagy, 1991; Szpakowska and Nagy, 1999; Muthuraman et al., 2009a):

$$C_F \xrightarrow{k_1} C_M \xrightarrow{k_2} C_S \tag{2.2}$$

where C_F, C_M, and C_S are the instantaneous solute concentrations in F, M, and S phases, respectively, and k_1 and k_2 are the apparent first-order rate constants of the extraction and stripping processes. According to Eq. (2.2), the rates of change of solute concentration in different phases are expressed as:

$$\frac{\mathrm{d}C_F}{\mathrm{d}t} = -k_1 C_F \tag{2.3}$$

$$\frac{\mathrm{d}C_M}{\mathrm{d}t} = k_1 C_F - k_2 C_M \tag{2.4}$$

$$\frac{\mathrm{d}C_S}{\mathrm{d}t} = k_2 C_M \tag{2.5}$$

Integration of Eqs. (2.3) to (2.5) leads to the time evolution expressions of solute concentrations in different phases:

$$C_F = C_{Fo} \exp(-k_1 t) \tag{2.6}$$

$$C_M = C_{Fo} \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \tag{2.7}$$

$$C_S = C_{Fo} \left\{ 1 - \frac{1}{k_2 - k_1} [k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \right\} \tag{2.8}$$

where C_{Fo} is the initial solute concentration in the F phase and t is the time elapsed. Dividing both sides of Eqs. (2.6) to (2.8) by C_{Fo}, it gives:

$$R_F = \exp(-k_1 t) \tag{2.9}$$

$$R_M = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{2.10}$$

$$R_S = 1 - \frac{1}{k_2 - k_1}[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \tag{2.11}$$

where $R_F = C_F/C_{Fo}$, $R_M = C_M/C_{Fo}$ and $R_S = C_S/C_{Fo}$, which are the reduced solute concentrations in F, M, and S phases, respectively. The relationship between the reduced solute concentrations in different phases is established as $R_F + R_M + R_S = 1$. By taking the first order time differentiation on Eqs. (2.9) to (2.11), the flux equations are obtained (Szpakowska and Nagy, 1991):

$$\frac{\mathrm{d}R_F}{\mathrm{d}t} = -k_1 \exp(-k_1 t) = J_F \tag{2.12}$$

$$\frac{\mathrm{d}R_M}{\mathrm{d}t} = \frac{k_1}{k_2 - k_1}[k_2 \exp(-k_2 t) - k_1 \exp(-k_1 t)] = J_M \tag{2.13}$$

$$\frac{\mathrm{d}R_S}{\mathrm{d}t} = \frac{k_1 k_2}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] = J_S \tag{2.14}$$

where J_F, J_M and J_S are the instantaneous fluxes of solutes in F, M, and S phases, respectively. When J_M (Eq. (2.13) is equal to zero, the maximum fluxes of solutes are achieved, which are given by:

$$J_F^{max} = -k_1 \exp(-k_1 t_{max}) \tag{2.15}$$

$$J_M = \frac{k_1}{k_2 - k_1}[k_2 \exp(-k_2 t_{max}) - k_1 \exp(-k_1 t_{max})] = 0 \tag{2.16}$$

$$J_S^{max} = \frac{k_1 k_2}{k_2 - k_1}[\exp(-k_1 t_{max}) - \exp(-k_2 t_{max})] \tag{2.17}$$

where J_F^{max} and J_S^{max} are the maximum fluxes of solutes in F and S phases, respectively, while t_{max} is the time at which maximum fluxes are reached. From Eq. (2.16), t_{max} is derived as (Szpakowska and Nagy, 1991):

$$t_{max} = \frac{\ln\left(\frac{k_1}{k_2}\right)}{k_1 - k_2} \tag{2.18}$$

Since J_M is equal to zero (Eq. 2.16), the system is at steady state and, hence, J_F^{max} (Eq. 2.15) and J_S^{max} (Eq. 2.17) are equal to each other but of opposite signs, that is $-J_F^{max} = J_S^{max}$. Substituting Eq. (2.18) into Eq. (2.10), the value of R_M at t_{max}, that is R_M^{max}, is obtained (Szpakowska and Nagy, 1991):

$$R_M^{max} = \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1 - k_2)} \tag{2.19}$$

The activation energy (E_a) of both extraction and stripping processes in liquid membrane can be determined from the Arrhenius equation (Yilmaz et al., 2008):

$$\ln k_i = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{2.20}$$

where k_i is either k_1 or k_2, A is the pre-exponential factor (frequency factor), R is the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K). In general, a process is diffusion-controlled if its E_a value is less than 20 kJ/mol, intermediate-controlled if E_a is between 20 and 50 kJ/mol and chemical reaction-controlled if it is more than 50 kJ/mol (Biswas et al., 2000).

2.2.4 Types and Comparison of Liquid Membranes

There are mainly three types of liquid membranes, namely, bulk liquid membrane (BLM), supported liquid membrane (SLM), and emulsion liquid membrane (ELM) (Boyadzhiev and Lazarova, 1995; Watson, 1999; Dutta, 2007). The former two are designed with no phase dispersion while the latter involves phase dispersion. These liquid membranes differ in their configurations and contacts between the F, M, and S phases. Figure 2.3 illustrates the schematic diagrams of some typical BLM, SLM, and ELM. In general, BLM has its F and S phases separated by a solid impermeable barrier while those of SLM are separated by the M phase which is immobilized in the pores of a microporous hydrophobic solid support. ELM, on the other hand, consists of water-in-oil emulsions formed by droplets of S phase contained in the M phase which are suspended or dispersed in the F phase.

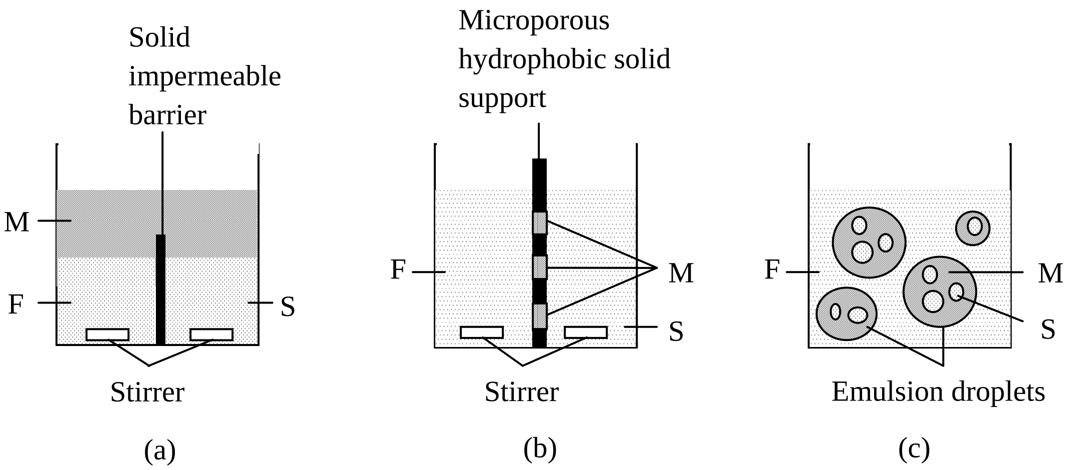


Figure 2.3 Schematic diagrams of some typical (a) BLM, (b) SLM and (c) ELM

A comparison among these liquid membranes in the aspects of design, manipulation, solvent inventory, fluxes, and membrane stability is presented in Table 2.2. BLM is the simplest type, easy to manipulate while offering good membrane stability. However, it shows relatively low fluxes due to its small interface area and long transportation path (Watson, 1999). In addition, the high solvent inventory of BLM tends to increase its material cost and poses an environmental hazard in the case of solvent loss, particularly when the solvent used is toxic. SLM and ELM, on the other hand, are more complicated systems, in which the former requires the impregnation of solvent on a microporous solid support while the latter involves a multistep process (Boyadzhiev and Lazarova, 1995). Being a non-dispersive liquid membrane like BLM, SLM is also relatively easy to manipulate. Conversely, ELM, a dispersive liquid membrane, which is susceptible to emulsion stability and requires the control of many parameters such as emulsification time and speed, surfactant concentration, and so forth (Sabry et al., 2007), is more difficult to manipulate. One of the outstanding features of SLM is its low solvent inventory due to the use of thin sheets of porous supports. Nevertheless, this gain is usually accompanied by a loss in the membrane stability due to the inevitable washing out of solvents from the pores of the support, which is mainly ascribed to lateral shear forces, progressive wetting, static pressure differential and osmotic pressure across the membrane (Hill et al., 1996; Zheng et al., 2009). Similar to BLM, SLM also exhibits relatively low fluxes due to its complex porous structure of the support which is accounted for by a specific tortuosity factor (Watson, 1999). There is a general belief that fluxes through SLM are larger than those through BLM (Watson, 1999). Nevertheless, several research works, which compared the metal ion fluxes through both the BLM and SLM under various operating conditions, reported that this belief was not always borne out by experiments (Szpakowska, 1996; Yang et al., 2003). ELM, on the contrary, provides the highest fluxes as a result of its extremely high interfacial area (Boyadzhiev and Lazarova, 1995). However, it often employs a considerable amount of solvents and suffers from poor emulsion stability. The latter is primarily affected by the membrane formulation, technique of emulsion preparation and conditions under which the emulsion is contacted with an external phase (Chiha et al., 2010; Ahmad et al., 2011).

Table 2.2 Comparison among different types of liquid membrane

	Types of Liquid Membrane		
Aspects	BLM	SLM	ELM
Design	Simple	Complicated	Complicated
Manipulation	Easy	Easy	Difficult
Solvent inventory	High	Low	High
Fluxes	Low	Low	High
Membrane stability	Good	Poor	Poor[a]

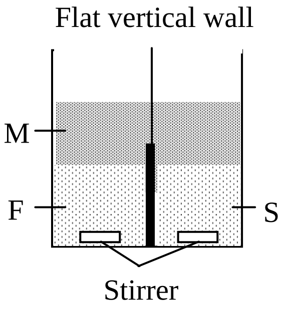
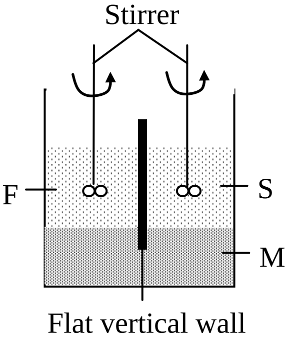
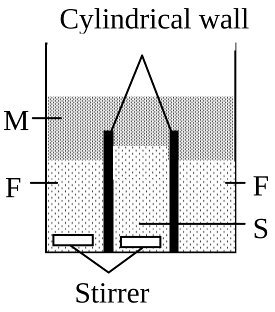
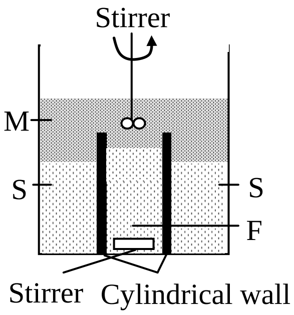
[a]Emulsion stability

2.2.5 Bulk Liquid Membrane

BLM is the simplest type of non-dispersive liquid membrane. It is broadly applied in laboratory studies on account of its characteristics such as constant interface area, constant hydrodynamic conditions, simple design, and ease of manipulation which make it a great tool for studying the kinetics, transport properties, and reaction mechanisms of various separation processes (Boyadzhiev and Lazarova, 1995).

BLM can be designed with a wide variety of configurations which, in most cases, consists of two parts: a common part containing the M phase and a separate part where the F and S phases are separated with or without a solid impermeable barrier. Table 2.3 presents the three regular types of BLM used by numerous researchers in various separation processes. They include those with a flat vertical wall, those with a cylindrical wall and those without any separating wall. These BLMs differ from each other in the shape of the solid impermeable barriers used, except for those without any separating wall. Some, if not all, of the phases are stirred with an appropriate intensity to avoid mixing between the phases. In any of these BLMs, the M phase is always in contact with the F and S phases and facilitates the transfer between them.

Table 2.3 Types of BLM

Types of BLM	References
(a) With flat vertical wall	
 	Yang and Fane, 1999; Gawroński and Reli, 2007; Chakrabarty et al., 2009
(b) With cylindrical wall	
 	Safavi and Shams, 1998, 1999a, 1999b; Krieg et al., 2000; He et al., 2000; Gong et al., 2002; Shamsipur et al., 2002; Granado-Castro et al., 2004; Aydiner et al., 2005;