RECOVERY OF KRAFT LIGNIN FROM PULPING WASTEWATER USING EMULSION LIQUID MEMBRANE PROCESS

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Specially dedicated to my Heavenly Father, beloved parents, family members and friends. Your endless love, support and prayers make it possible.

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ABSTRACT

Lignin represents a key sustainable source of biomass for transformation into biofuels and high-value specialty chemicals. Excess of lignin that imparts brownish dark coloration in pulping wastewater causes adverse pollution problems, hence affecting human. Therefore, there is a necessity for removal and recovery of lignin from wastewater. In this research, emulsion liquid membrane (ELM) technology has been applied. This study involved studies on liquid membrane formulation, stability of emulsion and extraction of lignin from simulated kraft lignin solution. An optimization of kraft lignin recovery from real pulping wastewater was performed using the response surface methodology (RSM). An ELM extraction model was developed to predict the extraction performance. The liquid membrane formulation was investigated on the choice of carrier, diluent and stripping agent using liquid-liquid extraction. ELM stability was determined at different surfactant concentrations, homogenizer speed, emulsifying time and agitation speed. Several important parameters governing the extraction process of lignin including concentration of carrier and stripping agents, treat ratio and extraction time were investigated. The liquid membrane formulation contains kerosene as a diluent, tricaprylmethylammonium chloride (Aliquat 336) as a carrier, sorbitan monooleate (Span 80) as a surfactant, 2- ethyl-1-hexanol as a modifer and sodium bicarbonate ($NaHCO_3$) as a stripping agent. The results depicted that the most stable emulsion was observed at 3 % (w/v) of Span 80, 12000 rpm of homogenizer speed, 5 min of emulsification time and 250 rpm of agitation speed. At the optimum condition of 10 min of extraction time, 0.007 M of Aliquat 336, 0.1 M of $NaHCO_3$ and 1:5 of treat ratio, the performance of extraction, stripping and recovery was 95%, 100% and 98% respectively in a one step process. The optimization by RSM showed that 97% of lignin was recovered at 0.012 M of Aliquat 336, 0.32 M of $NaHCO_3$ and 1:4.8 of treat ratio. In addition, the developed model was accepted to predict the kraft lignin extraction as the simulation results were consistent with the experimental result at the optimum condition. Therefore, ELM process is a promising technology to recover lignin from pulping wastewater while solving environmental problems simultaneously.

ABSTRAK

Lignin merupakan satu sumber utama biojisim yang berterusan untuk transformasi kepada bio bahan api dan bahan kimia khusus yang bernilai tinggi. Lebihan lignin yang memberikan warna coklat gelap dalam air sisa buangan proses pemulpaan menyebabkan masalah pencemaran yang serius dan seterusnya memberi kesan negatif kepada manusia. Oleh itu, penyingkiran dan perolehan semula lignin dari air sisa sangat diperlukan. Di dalam kajian ini, teknologi emulsi membran cecair (ELM) telah digunakan. Kajian ini melibatkan formulasi membran cecair, penstabilan emulsi dan pengekstrakan lignin daripada cecair kraft lignin simulasi. Pengoptimuman perolehan semula lignin dilakukan dengan menggunakan kaedah gerak balas permukaan (RSM). Model pengekstrakan ELM telah dibangunkan untuk meramalkan kebolehan pengekstrakan. Formulasi membran cecair telah dikaji ke atas pilihan agen pembawa, pelarut dan agen pelucutan dengan menggunakan pengekstrakan cecair-cecair. Kestabilan membran cecair ditentukan pada kepekatan surfaktan yang berbeza, kelajuan penghomogenan, masa pengemulsian dan kelajuan pengadukan. Beberapa parameter yang penting untuk mengawal proses pengekstrakan lignin telah dikaji termasuk kepekatan pembawa dan agen pelucutan, nisbah rawatan dan masa pengekstrakan. Formulasi membran cecair ini mengandungi kerosin sebagai bahan pelarut, tricaprylmethylammonia klorida (Aliquat 336) sebagai pembawa, sorbitan monooleate (Span 80) sebagai surfaktan, 2-etil-1-heksanol sebagai pengubahsuai dan natrium bikarbonat ($NaHCO_3$) sebagai agen pelucutan. Keputusan menunjukkan bahawa emulsi yang paling stabil didapati pada 3% (b/i) Span 80, kelajuan penghomogenan 12000 putaran per minit, masa pengemulsian 5 minit dan kelajuan pengadukan 250 putaran per minit. Pada keadaan optimum iaitu tempoh pengekstrakan 10 minit, 0.007M Aliquat 336, 0.1 M $NaHCO_3$ dan 1: 5 nisbah rawatan, prestasi pengekstrakan, pelucutan dan perolehan semula dalam satu langkah proses masing-masing adalah 95%, 100% dan 98%. Keadaan optimum yang diperolehi daripada RSM menunjukkan 97% lignin telah dihasilkan semula pada 0.012M Aliquat 336, 0.32M $NaHCO_3$ dan 1:4.8 nisbah rawatan. Di samping itu, model yang dibangunkan boleh diterima untuk meramalkan pengekstrakan lignin di mana keputusan simulasi adalah selari dengan keputusan ujikaji pada keadaan optimum. Oleh itu, proses ELM adalah berpotensi untuk mendapatkan semula lignin dari air sisa buangan proses pemulpaan di samping itu pada masa yang sama dapat menyelesaikan masalah alam sekitar.

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LIST OF ABBREVIATIONS

ELM	-	Emulsion Liquid Membrane
SLM	-	Supported Liquid Membrane
BLM	-	Bulk Liquid Membrane
LLE	-	Liquid-liquid Extraction
KL	-	Kraft Lignin
Aliquat 336	-	Tricaprylmethylammonium Chloride
Span 80	-	Sorbitan Monooleate
$NaHCO_3$	-	Sodium Bicarbonate
Na_2S	-	Sodium Sulfide
NaOH	-	Sodium hydroxide
NaCl	-	Sodium Chloride
Na_2CO_3	-	Sodium Carbonate
HCl	-	Hydrochloric Acid
H_2SO_4	-	Sulphuric Acid
Na_2SiO_3	-	Sodium silicate
F	-	Fisher
DF	-	Degree of freedom
MS	-	Mean Square
RSM	-	Response Surface Methodology
DOE	-	Design of Experiment
ANOVA	-	Analysis of Variance
SS	-	Sum-Squares
BBD	-	Box-Behnken Design
MATLAB	-	Matrix Laboratory
W/O	-	Water in Oil
O/W	-	Oil in Water

W/O/W	-	Water in oil in Water
HLB	-	Hydrophile-lipophile Balance
UV	-	Ultra-violet
RK	-	Runge-Kutta
ODEs	-	Ordinary Differential Equations
PDEs	-	Partial Differential Equations
FTIR	-	Fourier-transform infrared spectroscopy
LV	-	Low Viscosity
TOA	-	Trioctylamine
TDA	-	Tridodecylamine
Cyanex 302	-	Diisooctylthiophosphinic acid
D2EHPA	-	Bis(2-ethylhexyl) phosphate
TOPO	-	Tri-n-octylphosphine Oxide
TBP	-	Tributylphosphate
D	-	Distribution
Na^+	-	Sodium
K^+	-	Potassium
Ca^+	-	Calcium
Cl^-	-	Chloride
SO_4^{2-}	-	Sulfate

LIST OF SYMBOLS

meq	-	Milliequivalents
%	-	Percentage
M_n	-	Average molecular weight
M	-	Molar
rpm	-	Rotation per minute
w/v	-	Weight per volume
cP	-	Centipoise
g/ml	-	Gram per mililiter
mg/l	-	Milligram per liter
ppm	-	Part per million
nm	-	Nanometer
mL	-	Milliliter
ρ	-	Density
°C	-	Degree Celsius
min	-	Minutes
hrs	-	Hours
cm^{-1}	-	Per centimetre
[]	-	Concentration
$[KL]_i$	-	Initial concentration of kraft lignin in feed phase
$[KL]_f$	-	Final concentration of kraft lignin in feed phase
$[KL]_{int}$	-	Concentration of kraft lignin in internal phase after extraction
$[KL]_{mem}$	-	Concentration of kraft lignin in membrane phase after extraction
TR	-	Treat ratio

$V_{m,f}$	-	Volume of final membrane
$V_{m,i}$	-	Volume of initial membrane
V_{org}	-	Volume of organic phase
V_{ext}	-	Volume of external phase
r	-	Radial coordinate in the globule
$R_{m\mu}$	-	Radius of internal droplets
R_i	-	Radius of iner cole of W/O emulsion droplets
R	-	Radius of an emulsion globule
R_o	-	Initial radius of emulsion globules
S	-	Outer interfacial area of globules
S'	-	Internal interfacial area between membrane and internal droplets
N	-	Total number of emulsion globules
V_1	-	Volume of internal phase
V_2	-	Volume of membrane phase
V_3	-	Volume of external phase
V_1^0	-	Initial Volume of internal phase
V_{H20}	-	Partial molar volume of water
g	-	Osmotic coefficient
ϕ_1	-	Volume ratio of the internal phase in the emulsion drop
ϕ_2	-	Volume ratio of the emulsion to total volume of phases
C_{A3}	-	Concentration of KL in the external phase
C_{A3}^*	-	Concentration of KL in the external phase at the external-membrane interface
C_{A3}^0	-	Initial concentration of KL in the external phase
C_{A1}	-	Concentration of KL in the internal phase
C_{A1}^0	-	Initial concentration of KL in the internal phase
k_{OC}	-	External mass transfer coefficient
k_B	-	Rate of leakage
k_c	-	Mass transfer coefficients of C in the peripheral thin oil
k_b	-	Mass transfer coefficients of B in the peripheral thin oil
D_{ec}	-	Effective diffusivity of complex in emulsion phase
D_{eB}	-	Effective diffusivity of carrier in emulsion phase
C_C	-	Concentration of complex at the external-membrane

		interface
C_B	-	Concentration of carrier at the external-membrane interface
C_B^0	-	Initial concentration of carrier at the external-membrane interface
C_{S1}	-	Concentration of stripping agent in the internal phase
C_{S1}^0	-	Initial concentration of stripping agent in the internal phase
C_{s3}	-	Concentration of stripping agent in the external phase
r_s	-	Rate of stripping
m	-	Extraction distribution coefficient
q	-	Stripping distribution coefficient
r_e	-	Rate of extraction
r_s	-	Rate of stripping
Keq	-	Equilibrium constant
Di	-	External diffusivity
D_m	-	Diffusivity of complex in the aqueous phase
d_1	-	Diameter of propeller
d_t	-	Diameter of the tank
μ	-	Viscosity
R_e	-	Reynolds number

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Nowadays, the world encountered critical environmental problems. The increase in population and the rapidly increased demand for industrial development creates a lot of problems, such as over exploitation of resources and hence, lead to water pollution, as well as land and air environmental problems. The sources of water pollution came from various domestic and industrial effluents such as agriculture, cosmetics, foods and beverages, chemical, pharmaceutical, textile and pulping. Each industrial activity eliminates out its own type of wastewater. Wastewater discarded into the ecological system contains hazardous chemical substances such as heavy metals, organic pollutants and suspended solid that may cause harmful impact on human life and aquatic biota.

Wastewater produced from pulping industries is one of the significant water pollution sources. This industry is a very diverse sector in terms of raw materials, processes, products and equipment. It expands rapidly due to the development of advanced technology and the rise of market demand. Global production of pulp is expected to increase by 77% from 1995 to 2020 (OECD Environmental Outlook, 2001). Pulp industry utilizes a lot of fresh water which ranks third in the world, after the primary metal and chemical industries (Kallas and Munter, 1994). It becomes the sixth largest polluter of water bodies after oil, cement, leather, textile and steel industries (Ali and Sreekrishnan, 2000). The manufacture of pulp generates large volumes of wastewater (75% from water consumption) as high as 60 m^3/ton of pulp produced (Thompson *et al.*, 2001). These effluents will cause negative impacts on water quality including increases in colour, turbidity, toxicity, nutrient loads and addition of persistent compounds (Kirkwood *et al.*, 2001). The main concern of this effluent is discharged of brownish dark colored effluent. The abnormal coloration will cause reduction of photosynthesis on algal and aquatic plants due to limited transmittance of light into water bodies (Panchapakesan, 1991).

Lignin is the main constituent of pulp wastewater which imparts a dark coloration. It is the most abundant aromatic substances present in the biosphere. It is a naturally occurring amorphous, macromolecular biopolymer derived from wood structure of higher plants (Douglass, 1952). It acts as a binding agent to hold cells together, which are constituted by phenylpropanoid units linked to each other through a variety of non-hydrolysable C-O-C and C-C bonds. The fundamental precursors that build the structure of lignin are conyferil, sinaply and p-coumaryl alcohols. Annually, approximately 60 million metric tons of lignin are generated as a waste in the pulp industry alone (Li *et al.*, 2012). The amount of kraft lignin produced is the highest compared to other types of technical lignin because kraft process is the dominant pulping process in pulp mills with approximately 80% of the world chemical pulping production.

A by-product stream of this process known as black liquor, which consists of 34 wt% of lignin is normally burned for energy utilization to facilitate recovery of pulping chemicals (Mohan *et al.*, 2006). However, the recovery process is complicated and costly, which is not affordable for small industries. In addition, the recovery process that was implemented in industries will cause air pollution problems due to the emission of undesired gases such as release of carbon monoxide which will eventually cause global warming in the future. Thus, some alternative ways were discovered to replace the recovery process in order to preserve the environment.

Commonly, conventional biological methods used by pulp industries, such as aerated lagoons and activated sludge contribute in reducing COD load and toxicity, but these methods cannot effectively remove lignin from pulping wastewater (Doble and Kumar, 2005). Hence, various techniques have been investigated to remove the lignin compound from the effluent. The treatment methods include precipitation (Wang and Chen, 2013), coagulation (Tong *et al.*, 1999), electrocoagulation (Zaied and Bellakhal, 2009), activated sludge treatment (Zheng *et al.*, 2012), ultrafiltration (Liu *et al.*, 2004; Toledano *et al.*, 2010; Wallberg and Jönsson, 2006), photocatalytic degradation, degradation by white rot fungi (Wu *et al.*, 2005), ion exchange (Bassandeh *et al.*, 2013) , reverse osmosis (Chakravorty and Srivastava, 1987), electrolysis (Ghatak, 2009), and ozonation (Fontanier *et al.*, 2006). At present, the most popular and the oldest treatment methods are precipitation and coagulation. Some of the inherent disadvantages of these methods are time consuming, requires handling of a large amount of sludge, corrosive and non-eco-friendly. In addition, these methods are expensive and tedious, especially when operated on a large scale. Thus, industries are looking for competing alternative technologies can eliminate all of the mentioned disadvantages (Luong *et al.*, 2012).

One of the promising technologies is an emulsion liquid membrane (ELM) process. From the current knowledge, no attempts has been reported yet regarding the application of liquid membrane for kraft lignin removal from pulping wastewater generated by the kraft pulping process. Previously, liquid membrane technologies had been proposed as alternatives to the conventional treatment processes. It was successfully studied for removal and recovery of various solutes from wastewater including organic compounds such as alcohol (Chanukya and Rastogi, 2013), phenolic compounds (Garavand and Madadlou, 2014), phenylenediamine (Chuannan *et al.*, 2009), benzimidazole (Venkatesan and Meera Sheriffa Begum, 2009), dyes (Othman *et al.*, 2011), acetic acids (Lee and Hyun, 2010), metal ions such as zinc (Teresa *et al.*, 1993), lead (Sabry *et al.*, 2007), chromium (Bhowal *et al.*, 2012), and silver (Othman *et al.*, 2005; Othman *et al.*, 2006). It is a very promising and valuable method that offers several advantages such as ease of operation, large mass transfer area that leads to fast extraction and stripping, capable of applying carrier-mediated transport, low energy consumption, high efficiency, less consumption of expensive chemicals and high selectivity (Goyal *et al.*, 2011a). ELM could be competitive when the targeted species are present at low concentrations in aqueous solution.

1.2 Problem Statement

Recovery of kraft lignin from pulp industry becomes significant due to many applications of the final product. There is an economic assessment of chemical conversion technologies on lignin feed stock. Use of lignin in chemical conversions can cost as high as 1.08 US$/kg (Macfarlane *et al.*, 2009). Conversion of lignin into valuable products attracts interest in various industries. Value-added uses of lignin include conversion to aromatic chemicals or high-octane fuel additives, gasification to mixed alcohols and the production of lignin-based polymers and carbon fibre, which is an eco-friendly material (Holladay *et al.*, 2007; Stewart, 2008). For instance, it can be used in the production of biofuels, vanillin, animal feed pellets binder, pesticides, and others (Casas *et al.*, 2012).

Various processes have been developed for separation and purification of lignin from pulping liquor. The most common method used by pulp industries is precipitation by sulfuric or hydrochloric acid, followed by filtration and washing (Mussatto *et al.*, 2007). However, this method has an inherent drawback, which is colloid formation during precipitation. This will directly complicate the filtration process, resulting in low purity lignin (Toledano *et al.*, 2010). Other laboratory scale methods are ultrafiltration, nanofiltration, reverse osmosis, ion exchange, coagulation, electrocoagulation and activated sludge treatment (Liu *et al.*, 2004; Toledano *et al.*, 2010; Wallberg and Jönsson, 2006; Wang and Chen, 2013; Zaied and Bellakhal, 2009).

Recently, liquid membrane technology is considered as an advanced alternative process to concentrate and purify macromolecular species in waste aqueous solutions. This application has not yet been succeeded to be applied in the pulp industry, which is removal of lignin. Though, some researchers are trying to put their effort to examine an efficient liquid membrane separation process for the treatment of pulp mill effluent. The performances on removal of lignosulfonates using an emulsion liquid membrane (ELM), supported liquid membrane (SLM) and bulk liquid membrane (BLM) from its aqueous solution were investigated (Chakrabarty *et al.*, 2009b). According to this research, the results obtained were very promising. However, removal of kraft lignin from kraft pulping industry, which dominates the world, has not yet been investigated. Therefore, Emulsion Liquid Membrane (ELM) process is proposed in this research to recover kraft lignin from pulping wastewater.

In the ELM process, an organic phase that is immiscible with water containing carrier which is selective towards targeted solute, is interposed between two aqueous phases (external and internal phases). The main advantages of the ELM process are both extraction and stripping steps are combined in one stage, which leads to simultaneous purification and concentration of the solute. Therefore, during the process, the wastewater will be purified and lignin will be recovered and concentrated in the internal phase. Despite of many advantages of ELM, this technology has rarely been applied in the industry due to certain limitations such as loss of extraction efficiencies that often occurred in these systems due to lack of stability of emulsion globules (Chanukya and Rastogi, 2013). Commonly, stability problems that take place in an ELM system are swelling and breakage phenomena. Therefore, the combination effect of both emulsion swelling and breakage, namely ‘apparent swelling’, was investigated in this study.

In order to obtain a stable emulsion and effective lignin recovery, the selectivity of the membrane formulation, includes carrier, diluent, surfactant and stripping agent, is very crucial. In this research, the liquid membrane was prepared by dissolving carrier tricaprylmethylammonium chloride (Aliquat 336) and hydrophobic surfactant sorbitan monooleate (Span 80) in kerosene (diluent) with sodium bicarbonate ($NaHCO_3$) as the internal stripping phase and 2- ethyl-1-hexanol as the modifier. In order to implement this recovery method to pulp industry, optimization was carried out using response surface methodology and the ELM on kraft lignin removal was investigated based on the model developed and considering emulsion swelling and breakage effects on ELM.

1.3 Objectives

The primary objective of this research is to investigate the feasibility of an emulsion liquid membrane (ELM) system for recovery of lignin from pulp effluents. The study consists of three parts, which include liquid membrane formulation, emulsion liquid membrane stability and performance and recovery of lignin from real pulping wastewater. In summary, the objectives that are being studied in this research are:

i. To determine suitable liquid membrane component for kraft lignin extraction.
ii. To study the effect of emulsion swelling and breakage on performance of lignin extraction.
iii. To investigate the parameters affecting the efficiency of lignin extraction and recovery.
iv. To optimise the recovery of kraft lignin from real pulping wastewater using RSM method.
v. To validate the experimental results with the simulation results.

1.4 Scopes of the Study

In order to successfully formulate liquid membrane component for lignin removal, liquid-liquid extraction (LLE) was carried out with various types and concentrations of carrier, diluents and stripping agents. The parameters that will be studied are selection of carrier, solvent and stripping agent, effect of carrier concentrations (0.003-0.1M) and stripping agent concentrations (0.1-1.5M).

The second objective is focusing on the parameters for emulsion stabilization. Investigation on stability of primary emulsion was carried out through manipulating the concentration of surfactant (1 to 7% (w/v)), homogenizer speed (10000 to 16000 rpm) and emulsifying time (3-10 min). The influence of these factors on the emulsion drop size distribution and viscosity of the organic phase was determined under the microscope and viscometer, respectively. Meanwhile, swelling or breakage effect and extraction performance for double emulsion were investigated on parameters mentioned above with the agitation speed (125-450 rpm).

The performance of lignin extraction in ELM attained by a hydrodynamic condition in batch custom-built agitation column is based on some effects of the parameters. These parameters include extraction time (3-20 min), carrier concentration (0.005-0.03M), stripping agent concentration (0.01-1 M) and treat ratio (1:3-1:10). An investigation on the influences of different factors was conducted using traditional approach experiments, where one factor is changed whilst keeping the other constant. These parameters were carried out to determine the optimum condition for simulated wastewater. Meanwhile, range of the most significant parameters was determined for the next objective.

In order to optimize the influencing parameters on the performance of kraft lignin recovery from real pulping wastewater, RSM was implemented. Therefore, a statistical experimental design was investigated to optimize the process parameters including carrier concentration (0.006-0.015M), stripping agent concentration (0.5-0.35M) and treat ratio (1:3-1:10). A total of 15 experiments were required based on the design of experiment (DOE) created by using Statistica 8.0 (Stat Soft). Equations were validated by the statistical tests known as the analysis of variance (ANOVA). Response surfaces were plotted to determine individual and interactive effects of test variables on the percentage recovery of kraft lignin. In order to study the removal of lignin from real waste, waste characterization of real pulping effluent was carried out to determine the lignin structure, lignin concentration, metal content, ion content, pH, viscosity and density.

The experimental result of optimum condition was validated with simulation results of the general ELM mathematical models that developed based on study of Biscaia *et al.* (2001) and Othman (2006) with some modifications and assumptions in order to examine the validity of the proposed model. The model was developed by using MATLAB software, and the mathematical equation was solved using built-in function of MATLAB known as ‘ode45’. The effects of initial feed concentration, agitation speed and treat ratio were investigated using the proposed model.

1.5 Significance of the Study

Due to the great importance of lignin in environmental and economic consideration, it is essential to remove and recover lignin from wastewater on pulping industry. ELM process was implemented as promising alternative technology for overcoming the disadvantages of existing conventional treatments. It has tremendous advantages of simple operation, large mass transfer area that leads to fast extraction and stripping process in one step, less consumption of expensive chemicals and low operation cost. Besides, the large volume of effluent generated by pulping industry could be recycled for other purpose after lignin was removed and consequently conserves the environment. The developed mathematical model is crucial for application of ELM process on removal of lignin from wastewater on pulping industry in future.

1.6 Thesis Outline

This research contains five chapters, which presented the research in a sequential order. In the first chapter a brief introduction of the research backgrounds, problem statement, significance of study, research objective and scopes were presented. Chapter 2 presented detailed reviews of pulping process, characteristic of pulping wastewater and current wastewater treatment, lignin and its application, liquid membrane technology, RSM and ELM modelling. Then, in Chapter 3, the research methodology including selection of liquid membrane components using LLE, ELM extraction and recovery, optimization using RSM, modelling and analytical procedures was depicted. Afterwards, results and discussions were analysed and discussed well in Chapter 4. Experimental data collections were evaluated and analysed in detailed. The experimental results were validated with the simulation results for model validity. Finally, the conclusion and recommendation for future work were suggested in Chapter 5.

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