

Full paper

# Numerical Prediction Performance of Kraft Lignin Extraction Using **Boundary Breakage Model**

Zing-Yi Ooia, Norasikin Othmana,b\*, Chan Nyuk Yana

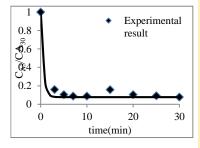
Centre Of Lipids Engineering and Applied Research (CLEAR), Ibnu Sina Insititute for Industrial and Scientific Research (IBNU SINA ISIR), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia

<sup>b</sup>Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor Malaysia

#### Article history

Received: 2 March 2015 Received in revised form: 24 April 2015 Accepted: 10 May 2015

## Graphical abstract



This study predicts the performance of kraft lignin extraction using emulsion liquid membrane (ELM) from pulping wastewater using boundary breakage model. The model was developed based on the previous study with some modifications and assumptions. Therefore, in developing kraft lignin extraction model, it will consider emulsion globule approach and the emulsion swelling and breakage during the ELMs process. It was found to be numerically stable and reliable in predicting the behavior of kraft lignin extraction using ELM for long duration of time. MATLAB software was used to predict the performance of ELM on extracting kraft lignin from pulping wastewater based on the model developed. At optimum condition, the simulation prediction result was found to have a small deviation with the experimental data on extraction efficiency. The model was computed with some parameter effects including initial feed concentrations; treat ratio and agitation speed, which demonstrated that the prediction results were in agreement with the theoretical study of ELM. The data instills confidence in the model as a useful prediction model on kraft lignin removal by ELM process in pulping industry.

Keywords: Emulsion liquid membrane; kraft lignin extraction; boundary breakage model, Pulping

© 2015 Penerbit UTM Press. All rights reserved.

## ■1.0 INTRODUCTION

Lignin is the main constituent that is responsible for the colour effluent in pulp industries. It is a natural amorphous polymer normally derived from the wood structure of higher plants. It acts as a binding agent to hold cells together. Annually, approximately 60 million metric tons of lignin are generated as a waste in the pulp industry alone [1]. Unfortunately, it has been identified as the sixth largest polluter industry discharging highstrength wastewater that is not only a serious aesthetic problem, but also hinders the algal and aquatic plant productivity by limiting light transmittance [2].

Hence, various techniques have been investigated to remove the lignin compound from the effluent. The treatment methods include precipitation [3] and coagulation, electrocoagulation [4], activated sludge treatment [5], ultrafiltration [6-8], reverse osmosis [9], electrolysis, and ozonation. At present, the most popular and oldest treatment methods are precipitation and coagulation. Some of the inherent disadvantages of these methods are time consuming, expensive, tedious, requires handling of a large amount of sludge, corrosive and non-eco-friendly. Thus, industries are looking for competing alternative technologies that eliminate all the mentioned disadvantages [10].

Liquid membrane technologies have been proposed as alternatives to the conventional treatment processes [11-13]. ELM was invented about 40 years ago [14]. It has been successfully studied for removal and recovery of various solutes from wastewater including organic compounds such as alcohol [15], phenolic compounds [16], phenylenediamine [17] and benzimidazole [18], dyes [19] and acetic acids [20], metal ions such as zinc[21], lead [22], chromium [23], and silver [24, 25].

ELM is a simple technique that combines the extraction and stripping steps in a one-step process. Water in oil (W/O) emulsion is formed by mixing two immiscible liquids where the internal aqueous phase encapsulated in the membrane oil phase and stabilized by surfactant. Then, this emulsion will be dispersed into the external phase and form water in oil in water (W/O/W) emulsion. In the present paper, simulated pulping wastewater is the external phase to be treated. The main advantages of the ELM process are large mass transfer area, capable of applying carrier-mediated transport and able to treat a variety compound in short time, which resulted in a high degree of effectiveness [26]. However, liquid membrane permeation is usually accompanied by the occurrence of some non-idealities such as swelling and breakage of emulsion.

In order to get a reliable mathematical formulation of ELM valid for long time periods, the breakage rate and the swelling of

<sup>\*</sup>Corresponding author: norasikin@cheme.utm.my

the globules have to incorporate into model which was harder to solve. The model was developed based on study of Biscaia *et al.* [27] and Othman [28] with some modifications and assumptions. Swelling occurs during the prolonged contact with the feed stream, leading to the change in the volume of emulsion and internal phase results in dilution of the stripping phase and consequent enlargement of globules. Hence, the membrane breakage happens and the concentrated solute in internal phase spill out into the external phase. This mathematical model of transport phenomenon in ELM system has been developed based on the below assumptions by considering the breakage and swelling of emulsion:

- The size of both globules and internal droplets are spherical and uniform in size and distribution that can be expressed as Sauter mean diameter.
- ii. The internal aqueous phase droplets are immobilized by sufficient amount of surfactant and thus there is no internal circulation inside the globule
- iii. The extraction by non-facilitated transport and diffusion of complexes itself without carrier is negligible.
- iv. There is no coalescence and re-dispersion of emulsion globules.
- The chemical reaction rate is much faster than diffusion within the globule. Thus local reaction equilibrium applies throughout the globules.
- vi. The distribution coefficient at the external interface between external and membrane phases is equal to that at the internal interface between membrane and internal phases.
- vii. The external phase is well mixed. Mass transfer resistance in this phase is restricted to the external boundary layer surrounding the globules.
- viii. The internal mass transfer resistance is negligible since it is so small in size of the droplets.
- ix. The process is isothermal at perfect mixing and all physical properties are constant during extraction. No loss of complex and carrier to the aqueous phases is considered.
- x. The pH value is remaining constant throughout the process in the external aqueous phase.
- xi. The number of (W/O/W) emulsion globules remains constant although swelling and breakage of the droplets are considered. The membrane breakage is assumed to occur at the outermost droplets of the globules. Hence, the film of membrane (insoluble in the aqueous phase) that covers these outermost droplets will not resist and will break but the number of globules still remains constant over time.

The objective of the present study is to predict the performance of kraft lignin extraction by ELM and compared with experimental results to test the validity of model.

#### 1.1 Extraction Mechanism of Kraft Lignin

The mechanism of carrier facilitated transport extraction and stripping process of kraft lignin (KL) by Aliquat 336 is shown in Figure 1. It is a cationic extractant in the chloride form. Prior to the extraction reaction, Aliquat 336 is transformed into the bicarbonate form in a certain ratio by contacting the membrane solution containing Aliquat 336 with stripping solution that contains NaHCO<sub>3</sub> as shown by Equation (1).

$$AQ^{+}Cl^{-} + NaHCO_{3} \Leftrightarrow AQ^{+}HCO_{3}^{-} + Cl^{-} + Na^{+}$$
(1)

During the extraction process, KL is transferred in its anionic form by a driving force resulting from the gradient of other anionic counter-ions between the two aqueous phases. KL ion chemically reacts with the carrier to form the KL-carrier complexes, AQKL on the external interface as illustrated by Equations (2) and (3).

Feed-membrane side reaction:

$$\begin{array}{l} AQ^+Cl^-\left(org\right) + KLNa(aq) \Leftrightarrow AQKL(org) + NaCl(aq) & (2) \\ AQ^+HCO_3^-\left(org\right) + KLNa(aq) \Leftrightarrow AQKL(org) + NaHCO_3(aq) & (3) \end{array}$$

Then, these complexes diffuse through the liquid membrane to the internal interface. In the presence of NaHCO<sub>3</sub>, the following reaction is expected to take place at the membrane phase on the stripping solution side.

Stripping-membrane side reaction:

$$AQKL(org)+ NaHCO_3(aq) \Leftrightarrow KLNa(aq) + AQ^+HCO_3^-(org)$$
(4)

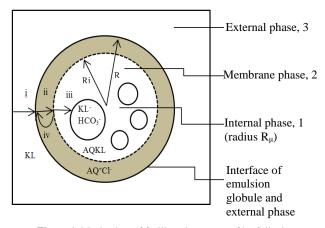


Figure 1 Mechanism of facilitated transport of kraft lignin

#### ■2.0 EXPERIMENTAL

#### 2.1 Chemicals and Reagents

Extractant tricaprylylmethylammonium chloride (Aliquat 336) was obtained from Acros. Sorbitan monooleate (Span 80) as a nonionic surfactant and 2- ethyl-1-hexanol as a modifier were obtained from Fluka (Buchs, CH). Kerosene as a diluent was procured from Sigma (St. Loius, MO, USA). Sodium bicarbonate (NaHCO<sub>3</sub>) as a stripping agent was obtained from Merck (Darmstadt, Germany). Kraft lignin was procured from Sigma. All chemicals and reagents used were of analytical reagent grade.

#### 2.2 Emulsion Preparation and ELM Extraction

10 mL of emulsion was prepared with 1:1 ratio of organic phase to aqueous internal stripping phase. The organic phase consisted of surfactant (Span 80), extractant (Aliquat 336), modifier (2-ethyl-1-hexanol) and diluent (kerosene). It was homogenized using Heidolph Silent Crusher M Emulsifier at the speed of 12,000 rpm for 5 min while the stripping agent (NaHCO<sub>3</sub>) was added dropwise to form a stable milky white primary emulsion. The emulsion must be freshly prepared each time prior to the experiments.

The primary emulsion was dispersed into an agitated vessel containing pulping wastewater (100 ppm of kraft lignin) with the appropriate treat ratio. The mixture was agitated at 250 rpm for 10 min. In order to obtain the optimum conditions in the extraction of emulsion liquid membrane, one variable was changed whilst the other conditions remained constant, which is listed in Table 1. Subsequently, the samples were quickly introduced into a separating funnel and left for phase separation within 15-30 min until the two layers of aqueous and emulsions were clearly separated. The sample of treated aqueous solution at the bottom was carefully separated from the emulsion, and the concentration was measured. All measurements were carried out in triplicate, and all data presented were averaged values. The extraction performance of the ELM was measured using Equation (5).

Percentage of Extraction, 
$$E = \frac{[\text{Kraft Lignin}]_i - [\text{Kraft Lignin}]_f}{[\text{Kraft Lignin}]_i} \times 100 \tag{5}$$

Where, [Kraft Lignin] is the initial concentration of kraft lignin in the feed phase (mg/L). [Kraft Lignin]f is the final concentration of kraft lignin in the feed phase (mg/L).

#### ■3.0 RESULTS AND DISCUSSION

#### 3.1 Mass Transfer Model

Based on the assumptions and transport mechanism by reaction on Equations (2) and (4), the governing equations for the extraction processes are:

i. Mass balance of solute in the external phase: 
$$V_3 \frac{dC_{A3}}{dt} = -k_{OC} \frac{3(V_1 + V_2)}{R} \left( C_{A3} - {C_{A3}}^* \right) + k_B C_{A1} V_1 \tag{6}$$

Where, CA3 is the concentration of KL in the external phase (mg/l), CA3\* is the concentration of KL in the external phase at the external-membrane interface (mg/l), CA30 is the initial concentration of KL in the external phase (mg/l), k<sub>OC</sub> is the external mass transfer coefficient (m/s), V<sub>1</sub> is the volume of internal phase (ml), V<sub>2</sub> is the volume of membrane phase (ml), V<sub>3</sub> is the volume of external phase (ml), R is the radius of an emulsion globule (m), k<sub>B</sub> is the rate of leakage and C<sub>A1</sub> is the concentration of KL in the internal phase (mg/l).

#### ii. Mass fluxes at the external-membrane interface

At the interface of the external-membrane, there is no accumulation of the solute at the interface. Thus, the flux of mass transfer outside the external-membrane interface is equal to the flux of mass diffusion inside the external-membrane interface was shown in Equation 7. The concentration of solute in external phase, CA3 is greater than that on external-membrane interface, CA3\*. The driving force to overcome external film resistance is the gradient of these two concentrations.

$$N(4\pi R^2)D_{eC}\left(\frac{\partial C_C}{\partial r}\right)_{r=R} = N(4\pi R^2)k_{oc}(C_{A3} - {C_{A3}}^*) \eqno(7)$$

Equilibrium:  $C_C^* = mC_{A3}^*$ 

Where, N is the total number of emulsion globules ,R is the radius of an emulsion globule, Dec is the effective diffusivity of complex in emulsion phase (m<sup>2</sup>/s), C<sub>C</sub> is the concentration of complex at the external-membrane interface (mg/l), koc( CA3CA3\* ) is the flux of mass transfer outside external-membrane interface,  $D_{eC}\left(\frac{\partial C_c}{\partial r}\right)_{r=R}$  is the flux of mass diffusion inside external-membrane interface and m is the extraction distribution coefficient.

iii. Mass transfer of carrier and complex within emulsion globules  $0 \le r \le Ri$ .

The mass balance equations of the carrier B and the complex C in the region of 0≤r≤Ri within the emulsion drop are expressed by the effective diffusivities of complex and carrier, Dec and DeB in Equations (8) and (9).

$$\begin{split} \frac{\partial C_{C}}{\partial t} &= \frac{(V_{1} + V_{2})_{i}}{V_{2}} D_{ec} \left( \frac{1}{r^{2}} \frac{\partial}{\partial r} \left( r^{2} \frac{\partial C_{C}}{\partial r} \right) \right) - \frac{S' r_{s}}{V_{2}} \\ \frac{\partial C_{B}}{\partial t} &= \frac{(V_{1} + V_{2})_{i}}{V_{2}} D_{eB} \left( \frac{1}{r^{2}} \frac{\partial}{\partial r} \left( r^{2} \frac{\partial C_{B}}{\partial r} \right) \right) + \frac{S' r_{s}}{V_{2}} \end{split} \tag{8}$$

$$\frac{\partial C_B}{\partial t} = \frac{(V_1 + V_2)_i}{V_2} D_{eB} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_B}{\partial r} \right) \right) + \frac{S' r_s}{V_2}$$
(9)

Where, V<sub>1</sub> is the volume of internal phase (ml), V<sub>2</sub> is the volume of membrane phase (ml), V<sub>1</sub>+V<sub>2</sub> is the total volume of emulsion (ml), Cc is the concentration of complex at the external-membrane interface (mg/l), C<sub>B</sub> is the concentration of carrier at the external-membrane interface (mg/l), D<sub>ec</sub> is the effective diffusivity of complex in emulsion phase (m<sup>2</sup>/s), D<sub>eB</sub> is the effective diffusivity of carrier in emulsion phase (m<sup>2</sup>/s), r<sub>s</sub> is the rate of stripping and S' is the internal interfacial area between membrane and internal droplets (m<sup>2</sup>).

iv. Mass balance of solute and bicarbonate ion in the internal phase

$$\begin{aligned} V_{1} \frac{dC_{A1}}{dt} &= S'r_{S} - C_{A1} \frac{dV_{1}}{dt} - k_{B}C_{A1} \\ V_{1} \frac{\partial C_{S1}}{\partial t} &= -\frac{3V_{1}}{R_{mu}} r_{S} \end{aligned} \tag{10}$$

$$V_1 \frac{\partial C_{s_1}}{\partial t} = -\frac{3V_1}{R_{mu}} r_s \tag{11}$$

Equilibrium:  $C_{A1} = qC_C$ 

Where, V<sub>1</sub> is the volume of internal phase (ml), C<sub>A1</sub> is the concentration of KL in the internal phase (mg/l), q is the stripping distribution coefficient and R<sub>mu</sub> is the radius of emulsion droplets (m).

Initial and boundary conditions are expressed respectively as below:

Initial conditions:

 $C_{A3} = C_{A30} \quad C_{A1} = 0$ For t=0: For t=0,  $0 \le r \le Ri$ :  $C_C = 0$ ,  $C_B = C_B^0$ ,  $C_{A1} = C_{A1}^0$ ,  $C_{S1} = C_{S1}^0$ 

Boundary conditions: For t $\geq$ 0, r=0:  $\frac{\partial C_C}{\partial r} = \frac{\partial C_B}{\partial r} = 0 \; ; C_C = \text{finite, } C_B = \text{finite}$ 

$$-D_{eB} \left( \frac{\partial C_{B}}{\partial r} \right) + \varphi_{1}^{\frac{2}{3}} r_{s} = D_{eC} \left( \frac{\partial C_{C}}{\partial r} \right) + \varphi_{1}^{\frac{2}{3}} r_{s}$$

$$= k_{b} (C_{B}|_{r=Ri} - C_{B}|_{r=R}) = k_{C} (C_{C}|_{r=R} - C_{C}|_{r=Ri}) = r_{f}|_{r=R}$$
(12)

Where, kb and kc are the mass transfer coefficients of B and C in the peripheral thin oil layer respectively, CB0 is the initial concentration of carrier at the external-membrane phase (mg/l), CA10 is the initial concentration of KL in the internal phase (mg/l), C<sub>S1</sub> is the concentration of stripping agent in the internal phase,  $C_{S1}^{0}$  is the initial concentration of stripping agent in the internal phase and  $\phi_1$  is the volume ratio of the internal phase in the emulsion drop.

#### 3.2 The Swelling and Breakage Effect

The volume change of external phase and interfacial area were changed with the swelling and the breakage rate of the droplets. The transient superficial area and volume of N spherical (W/O/W) emulsion globules as a function of the emulsion globule radius is shown in Equations (13) and (14).

$$\begin{split} NS(t) &= 4\pi N R^2(t) = 3 \frac{V_1(t) + V_2}{R(t)} = 3 \left( \frac{V_1^0 + V_2}{R_0^3} \right) R^2(t) \\ V_3(t) &= V_1^0 + V_2 + V_3^0 - \left( \frac{V_1^0 + V_2}{R_0^3} \right) R^3(t) \end{split} \tag{13}$$

$$V_3(t) = V_1^{\circ} + V_2 + V_3^{\circ} - \left(\frac{V_1^{\circ} + V_2}{R^{\circ}}\right) R^3(t)$$
 (14)

Where, S is the outer interfacial area of globules (m<sup>2</sup>), N is the total number of emulsion globules, R is the radius of emulsion globules (m), R<sub>o</sub> is the initial radius of emulsion globule (m), V<sub>1</sub> is the volume of internal phase (m<sup>3</sup>), V<sub>2</sub> is the volume of membrane phase (m<sup>3</sup>) and V<sub>3</sub> is the volume of external phase

The breakage constant (kB) is included to account for the interfacial area of the internal droplets and the number of droplets in Equation (15). The change of interfacial area of the emulsion globules is depicted in Equation (16).

$$\frac{\mathrm{d}n(t)}{\mathrm{d}t} = -k_{\mathrm{B}}n(t) \tag{15}$$

$$\frac{dn(t)}{dt} = -k_B n(t)$$

$$S'(t) = \frac{3}{R_{\text{mu}}} \sqrt[3]{V_1^{\ 0} e^{-k_B t} \left[ \left( \frac{V_1^{\ 0} + V_2}{R_0^{\ 3}} \right) R^3(t) - V_2 \right]^2}$$
(15)

The kb value was studied by Nakashio et al., [29] which is range from 10<sup>-5</sup> to 10<sup>-6</sup> by sufficient amount of Span 80. The swelling occurred during which the radius of the emulsion liquid membrane was expanding. The rate of change of the radius depends on the average concentration of kraft lignin, carrier and stripping agent of in the system. Equation (17) displays the formula for change of radius. The transient volume of internal phase was developed in Equation (18).

$$\begin{split} \frac{dR}{dt} &= k_{OC} V_{H_{20}} \{ g_1 [C_{A1} + C_{s1}] - g_3 [C_{A3} + C_{s3}] \} \\ \frac{dV_1}{dt} &= 4\pi R^2 k_{OC} V_{H_{20}} \{ g_1 [C_{A1} + C_{s1}] - g_3 [C_{A3} + C_{s3}] \} \end{split} \tag{17}$$

Where, koc is the external mass transfer coefficient (m/s), V<sub>H20</sub> is the partial molar volume of water (m<sup>3</sup>/kmol), g is the osmotic coefficient, C<sub>S1</sub> is the concentration of stripping agent in the internal phase (mg/l), C<sub>s3</sub> is the concentration of stripping agent in the external phase (mg/l), R<sub>mµ</sub> is the radius of emulsion

The above set of equations is non-linear partial difference equations (PDEs). Some equations were too complicated to solve analytically. Therefore, numerical methods were applied to transform the PDEs to ordinary differential equations (ODEs). Thus, after simplification, all equations were solved simultaneously using MATLAB software by built in ode45 function.

#### 3.3 Model Parameters Estimation

All parameters required for the prediction can be classified into three categories. They are: (1) physical and chemical properties; (2) operating conditions; (3) diffusivity and mass transfer coefficient. The physical and chemical parameters were based on the experimental conditions as well as empirical correlations. Parameters were obtained from certain equations available include effective diffusivity, mass transfer coefficient, emulsion globules diameter, equilibrium constant, forward and backward extraction constant and distribution coefficient.

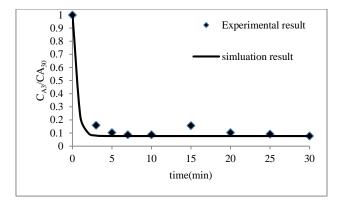
independently evaluated parameters were then incorporated into the mathematical models. Each parameter was calculated based on specific equation. The estimated value for each parameters and experimental parameters was listed in Table 1.

Table 1 Typical modeling parameters

Experimental parameters	Value
Initial Volume of internal phase, V <sub>1</sub> <sup>0</sup>	5ml
Volume of internal phase, $V_1$	5ml
Volume of membrane phase, V <sub>2</sub>	5ml
Treat Ratio, TR	0.2 (1:5)
Initial concentration of KL in the external phase, $C_{A3}^{0}$	100ppm
Initial concentration of KL in the internal phase,	0ppm
$C_{Al}^{0}$	**
Initial concentration of stripping agent in the	0.1M
internal phase, C <sub>S1</sub> <sup>0</sup>	
Initial concentration of carrier, C <sub>B</sub> <sup>0</sup>	0.007M
Treat ratio, TR	1:5
<b>Equilibrium Constant and Relative</b>	
Diffusivities	
Effective diffusivity of complex in the	$7.968x10^{-6}$
membrane phase(m²/min), <b>D</b> <sub>ec</sub>	
Mass transfer coeeficient (m/min), koc	0.069
Rate of breakage, $k_b(1/min)$	1 x 10 <sup>-5</sup>
$\Phi_1$ : volume ratio of the internal phase in the emulsion drop	0.5
$\Phi_2$ : volume ratio of the emulsion to total	0.0166
volume of phases	
Radius of emulsion droplets, $R_{m\mu}$	1.48x 10 <sup>-6</sup> m
Radius of emulsion globules, R	$5x10^{-4}m$
m: external distribution coeeficient	97.96
q: stripping distribution coefficient	0.98
Rate of extraction, re (mg/L.min)	23.73
Rate of stripping, rs (mg/L.min)	23.73
Equilibrium constant, Keq	290.87

#### 3.4 Validation of Model

The validity proposed model was investigated by comparing the results between experimental data and simulation results at optimum condition. These results will show the model reliability for kraft lignin extraction from pulping wastewater. The experimental results for kraft lignin removal by ELM, expressed in terms of  $C_{\rm A3}/C_{\rm A30}$  and time, are compared with the prediction results in Figure 2.



**Figure 2** Comparison between experimental data and model prediction (Experimental conditions [Span 80] = 3% (w/v), feed phase = 100 ppm kraft lignin solution, [Aliquat 336] = 0.007M, [NaHCO<sub>3</sub>] = 0.1 M)

The simulation results describe that the kraft lignin was extracted rapidly at the first 2 min and become stable after 3 min of extraction. However, there is slower extraction rate on experimental work which reaches equilibrium at 5 minutes. At 15 min of extraction there is slightly lower of extraction in experimental data. This may also due to the random errors which are from instrument or manual behavior in the experiments. From the results, the deviation was found to be 2.59%. This indicated that the computed model is compatible with the experimental results in removal of lignin using ELM. The standard mean deviation below 5% was acceptable also reported by Reis and Carvalho [30]. The small differences between the theoretical and experimental results may be due to errors in estimating the effective diffusivity. Besides, the polydisperse properties of the dispersed emulsion phase that neglected in this model may be one of the reasons in deviation. The model formulated in this work was emphasized by estimation of parameters by experimental independently or correlation equation, and there is no curve-fitting is required. The good agreement between the theoretical results and the experimental data instills confidence in the model as a useful prediction model for the analysis and interpretation of subsequent batch experimental results with some parameter effects.

#### 3.5 Modelling Results on Parameters Effect

#### 3.5.1 Effect of Initial Concentration of Kraft Lignin

The concentration gradient of kraft lignin in external and internal phase is the driving force for the extraction process. The initial concentration of kraft lignin was varied from 100 to 500ppm. The effect of initial concentration of kraft lignin on extraction rate is depicted in Figure 3.

From this finding, the higher feed concentration gives the lower extraction efficiency. The maximum extraction efficiency that achieved at 100 ppm, 500 ppm, 1000 ppm and 1500 ppm of

feed concentration were 95%, 93%, 86%, 76% respectively. It is noticeable that most amount of solute was extracted from feed solution with 100 ppm of feed concentration. The kaft lignin concentration in real pulping wastewater was fluctuated and depends on their pulping manufacturing stream. When the initial kraft lignin concentration increases, the length of diffusional path through the emulsion globule increases, since the internal droplets in the peripheral region are saturated more rapidly by lignin ion. Thus, more stripping agent is required to give a larger capacity of the emulsion for extraction. The complex must diffuse through the membrane phase to the more inner region of the drop to release lignin in the internal phase.

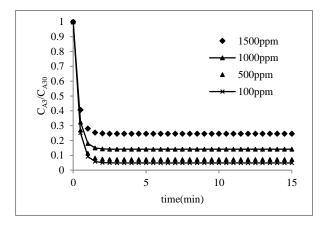


Figure 3 Effect of initial concentration of kraft lignin on KL extraction by model prediction

### 3.5.2 Effect of Treat Ratio

The volume ratio of emulsion phase to external phase plays crucial role in the treatment of effluents. Its variation cannot be random, because it is necessary to guarantee that the NaHCO<sub>3</sub> concentration that present in the internal phase is high enough to react with the external phase which is the kraft lignin solution. Figure 4 shows the effect of treat ratio on the extraction rate of KL by ELM.

The effect of volume ratio of emulsion to external phase to degree of extraction was enhanced by the increase of volume ratio. In addition, the extraction rate was faster by increase of volume ratio. At treat ratio 1:5, the maximum extraction reached at 2 min of extraction. However at treat ratio 1:20, it reached maximum of extraction at 5 min which is slower than higher treat ratio. The increase of volume ratio means more emulsion present as a whole towards external phase. Thus, the total number of emulsion globules increases and subsequently interfacial area between the external feed and emulsion phase increase. The capacity of internal phase for trapping lignin increased simultaneously. Hence, the mass transfer rate increased which enhance the degree of extraction and stripping. In addition, the amount of external phase increase cause the emulsion could not disperse well. Higher stirring speed should be used to enhance the dispersion. This is supported by Kumbasar and Sahin [31] that the extraction rate was increased with the increasing of treat ratio. Regarding to the point of view of industry, emulsion used must be considered very well to ensure the process to be economically feasible. Minimum volume of emulsion is preferred to treat large amount of wastewater. However, extraction efficiency should be considered as well.

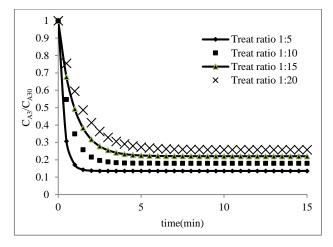


Figure 4 Effect of treat ratio on KL extraction by model prediction

#### 3.5.2 Effect of Agitation Speed

The power intensity delivered to the extractor from agitation plays a vital role in ELM process. The size of emulsion globules strongly depends on the mode and power of the mixing. Previous works had revealed increasing the level of agitation would increase the number of smaller globules while interact with aqueous solution [26, 32]. Figure 5 show the effect of agitation speed on kraft lignin extraction rate by ELM.

From the figure, the extraction rate increases as the agitation speed increases from 50 rpm to 250 rpm. At low agitation speed, larger emulsion globules are formed and produce less area for mass transfer. The extraction kinetics performs slower due to thicker boundary layer at interface of emulsion globules and stripping phase. The mass transfer coefficient (koc) increases with increasing of agitation speed. This is because at constant emulsion phase volume, the total mass transfer area increase as the globule size decrease that result in the increase in the total number of emulsion globules. However, further increase in the agitation speed to 300 rpm occured no increase in the degree of extraction. This result elucidate that 250 rpm was enough for the extraction process. Too vigorous mixing will cause high possibility of membrane breakage and concentrated solute will leak from the internal phase and eventually cause reduction of extraction efficiency which is undesirable. This was in agreement by Chakraborty et al. [33] that the sauter mean diameter of emulsion globules increase with increase of agitation speed from 500 to 700 rpm which resulted in higher extraction efficiencies.

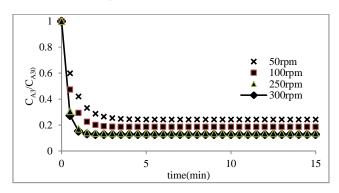


Figure 5 Effect of agitation speed on KL extraction by model prediction

#### ■4.0 CONCLUSION

The model was successfully solved numerically and analytically using MATLAB software. At optimum condition, the simulation prediction result was found to have a small deviation with the experimental data on extraction efficiency. The model was computed with some parameter effects including initial feed concentration; treat ratio and agitation speed, which demonstrated that the prediction results were in agreement with the theoretical study of ELM. The data instills confidence in the model as a useful prediction model on kraft lignin removal by ELM process in pulping industry.

#### Acknowledgement.

The authors would like to acknowledge Malaysia Ministry of Higher Education (MOHE), Centre of Lipid Engineering and Applied Research and Universiti Teknologi Malaysia (RU Research Grant; GUP:Q.J130000.7125.00H35) for the financial support to make this research possible.

#### References

- Li, S.-N. Sun, F. Xu and R.-C. Sun. 2012. Sequential Solvent Fractionation of Heterogeneous Bamboo Organosolv Lignin for Valueadded Application. Separation and Purification Technology. 101: 18– 25.
- [2] Ali, M. and T.R. Sreekrishnan. 2001. Aquatic Toxicity from Pulp and Paper Mill Effluents: A Review. Advances in Environmental Research. 5: 175–196.
- [3] Wang, G. and H. Chen. 2013. Fractionation of Alkali-extracted Lignin from Steam-exploded Stalk by Gradient Acid Precipitation. Separation and Purification Technology. 105: 98–105.
- [4] Zaied, M. and N. Bellakhal. 2009. Electrocoagulation Treatment of Black Liquor fFrom Paper Industry. *Journal of Hazardous Materials*. 163: 995–1000.
- [5] Zheng, Y., L.-Y. Chai, Z.-H. Yang, C.-J. Tang, Y.-H. Chen and Y. Shi. 2012. Enhanced Remediation of Black Liquor by Activated Sludge Bioaugmented with a Novel Exogenous Microorganism Culture. Applied Microbiology and Biotechnology. 97: 1–11.
- [6] Wallberg, O. and A.-S. Jönsson. 2006. Separation of Lignin in Kraft Cooking Liquor from a Continuous Digester by Ultrafiltration at Temperatures Above 100°C. *Desalination*. 195: 187–200.
- [7] Liu, G., Y. Liu, J. Ni, H. Shi and Y. Qian. 2004. Treatability of Kraft Spent Liquor by Microfiltration and Ultrafiltration. *Desalination*. 160: 131–141.
- [8] Toledano, A., A. García, I. Mondragon and J. Labidi. 2010. Lignin Separation and Fractionation by Ultrafiltration. Separation and Purification Technology. 71: 38–43.
- [9] Chakravorty, B. and A. S. Srivastava. 1987. Application of Membrane Technologies for Recovery of Water from Pulp and Paper Mill Effluents. *Desalination*. 67: 363–369.
- [10] Luong, N., N. Binh, L. Duong, D. Kim, D.-S. Kim, S. Lee, B. Kim, Y. Lee and J.-D. Nam. 2012. An Eco-friendly and Efficient Route of Lignin Extraction from Black Liquor and a Lignin-based Copolyester Synthesis. *Polymer Bulletin*. 68: 879–890.
- [11] Xian, C. K., N. Othman, N. Harruddin, N. A. Nasruddin and Z. Y. Ooi. 2014. Extraction of Lignosulfonate Using Toa-kerosene-Pvdf in Supported Liquid Membrane Process. *Jurnal Teknologi(Sciences and Engineering)*. 67: 59–63.
- [12] Ooi, Z. Y., N. Othman, M. Mohamad and R. Rashid. 2014. Removal Performance of Lignin Compound from Simulated Pulping Wastewater Using Emulsion Liquid Membrane Process. *International Journal of Global Warming*. 6: 270–283.
- [13] Yan, C. N., Othman N. and O. Z. Y. 2014. Prediction of Kraft Lignin Extraction Performance Using Emulsion Liquid Membrane Carrier-Diffusion Model. *Jurnal Teknologi*. 67: 17–21.
- [14] Li, N. N. 1971. Separation of Hydrocarbons by Liquid Membrane Permeation. *Industrial & Engineering Chemistry Process Design and Development*. 10: 215–221.

- [15] Chanukya, B. S. and N. K. Rastogi. 2013. Extraction of Alcohol From Wine and Color Extracts Using Liquid Emulsion Membrane. Separation and Purification Technology. 105: 41–47.
- [16] Garavand, F. and A. Madadlou. 2014. Recovery of Phenolic Compounds from Effluents by a Microemulsion Liquid Membrane (mlm) Extractor. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 443: 303–310.
- [17] Chuannan, L., X. Zhongpeng, W. Xueying and L. Zhen. 2009. Extraction of p-phenylenediamine from Aqueous Solutions Using Emulsion Liquid Membranes. In 3rd International Conference On Bioinformatics and Biomedical Engineering. Beijing.
- [18] Venkatesan, S. and K. M. Meera Sheriffa Begum. 2009. Emulsion Liquid Membrane Pertraction of Benzimidazole Using a Room Temperature Ionic Liquid (rtil) Carrier. Chemical Engineering Journal. 148: 254–262.
- [19] Othman, N., S. N. Zailani and N. Mili. 2011. Recovery of Synthetic Dye from Simulated Wastewater Using Emulsion Liquid Membrane Process Containing Tri-Dodecyl Amine as a Mobile Carrier. *Journal of Hazardous Materials*. 198: 103–112.
- [20] Lee, S.C. and K.-S. Hyun. 2010. Development of an Emulsion Liquid Membrane System for Separation of Acetic Acid from Succinic Acid. *Journal of Membrane Science*. 350: 333–339.
- [21] Teresa, M., A. Reis and J. M. R. Carvalho. 1993. Recovery of Zinc from an Industrial Effluent by Emulsion Liquid Membranes. *Journal of Membrane Science*. 84: 201–211.
- [22] Sabry, R., A. Hafez, M. Khedr and A. El-Hassanin. 2007. Removal of Lead by aAn Emulsion Liquid Membrane: Part I. Desalination. 212: 165-175
- [23] Bhowal, A., G. Bhattacharyya, B. Inturu and S. Datta. 2012. Continuous Removal of Hexavalent Chromium by Emulsion Liquid Membrane in a Modified Spray Column. Separation and Purification Technology. 99: 69–76.
- [24] Othman, N., H. Mat and M. Goto. 2006. Separation of Silver from Photographic Wastes by Emulsion Liquid Membrane System. *Journal* of Membrane Science. 282: 171–177.

- [25] Othman, N., H. Mat and M. Goto. 2005. Selective Extraction of Silver from Liquid Photographic Waste. Solvent Extraction Research and Development-Japan. 12: 27–34.
- [26] Sahoo, G. C. and N. N. Dutta. 1998. Studies on Emulsion Liquid Membrane Extraction of Cephalexin. *Journal of Membrane Science*. 145: 15–26.
- [27] Biscaia Junior, E. C., M. B. Mansur, A. Salum and R. M. Z. Castro. 2001. A Moving Boundary Problem and Orthogonal Collocation in Solving A Dynamic Liquid Surfactant Membrane Model Including Osmosis And Breakage. *Brazilian Journal of Chemical Engineering*. 18: 1–17.
- [28] Othman, N. 2006. Selective Emulsion Liquid Membrane Extraction of Silver from Liquid Phtographic Waste Industries. Universiti Teknologi Malaysia.
- [29] Nakashio, F., M. Goto, M. Matsumoto, J. Irie and K. Kondo. 1988. Role of Surfactants in the Behavior of Emulsion Liquid Membranes — Development of New Surfactants. *Journal of Membrane Science*. 38: 249–260.
- [30] Reis, M. T. A. and J. M. R. Carvalho. 2004. Modelling of Zinc Extraction from Sulphate Solutions With Bis(2-Ethylhexyl)Thiophosphoric Acid by Emulsion Liquid Membranes. Journal of Membrane Science. 237: 97–107.
- [31] Kumbasar, R. A. and İ. Şahin. 2008. Separation and Concentration of Cobalt from Ammoniacal Solutions Containing Cobalt and Nickel by Emulsion Liquid Membranes Using 5,7-Dibromo-8-Hydroxyquinoline (dbhq). *Journal of Membrane Science*. 325: 712–718.
- [32] Datta, S., P. K. Bhattacharya and N. Verma. 2003. Removal of Aniline from Aqueous Solution in a Mixed Flow Reactor Using Emulsion Liquid Membrane. *Journal of Membrane Science*. 226: 185–201.
- [33] Chakraborty, M., C. Bhattacharya and S. Datta. 2003. Effect of Drop Size Distribution on Mass Transfer Analysis of the Extraction of Nickel(Ii) by Emulsion Liquid Membrane. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 224: 65–74.