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Prediction of Kraft Lignin Extraction Performance Using Emulsion Liquid Membrane Carrier-Diffusion Model

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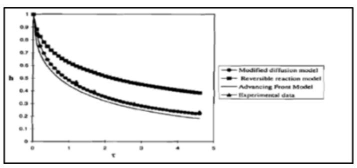
Graphical abstract



Abstract

This study presents the model to predict the performance of emulsion liquid membrane (ELM) to extract kraft lignin. Kraft lignin is one of the raw material that can be convert into biodiesel and also applied in producing large amount of chemical product such as vanillin. ELM is a separation method which can separate component without mechanical support. In this study, ELM model was developed and solved using MATLAB software. Three parameters were investigated in this study such as treat ratio, carrier concentration and initial concentration of feed phase. The study shows that ELM performs best at treat ratio of 1:5, concentration carrier of 0.3M and 0.5g/L of initial concentration of feed phase.

Keywords: Emulsion liquid membrane; kraft lignin; carrier-mediated; model; swelling

1.0 INTRODUCTION

Nowadays, everyone concern on pollution issue and emphasize about bio-products that are environmental friendly. Fuel is one of the non-renewable sources which are widely used in large amount and cause air pollution. In order to reduce the use of fuel that may cause pollution to our Earth, biofuel is introduced to reduce the usage of fossil fuel. Thus, a renewable source known as kraft lignin that is removed from wood or pulping process is introduced in this research.

Kraft lignin is one of the important components of wood [1] which can be as fuel application where the burning of lignin produces more than sufficient energy to operate the pulping plant. Furthermore, lignin can also be applied into an array of high-value-added products such as carbon fibres and phenols that is used in phenol-formaldehyde resin and also can be applied in production of lignin-based chemical such as vanillin and dispersing agents.

Chakraborty *et al*. reported that membrane separation is a good separation method due to its simple technique that can extract out components without mechanical support and low energy consumption [2]. Liquid membrane is widely used in many fields. For example, ELM can be used to extract metal ions such as copper [3], zinc [4], cadmium[5], cobalt, nickel [6] and other noble metals such as gold [7] and silver [8]. There are three types of liquid membranes such as bulk liquid membrane, supported liquid membrane and emulsion liquid membrane. Emulsion liquid membrane (ELM) is also known as liquid surfactant membrane or double emulsion. Kargari *et al.* stated that ELM consists of triple emulsion system that is water-in-oil-in-water(W/O/W) or oil in water in oil (O/W/O) which is separated with each other [7].
There are three types of transport model for ELM system includes simple diffusion, diffusion type mass transfer models for Type I facilitation and carrier mediated transport models for Type II facilitation. In this study, carrier mediated transport models for Type II facilitation is used to extract kraft lignin from pulping waste because kraft lignin can be removed with the presence of carrier more efficiency. Chakraborty *et al*. stated that in this model, a carrier or known as complexing agent is used to react with solute to form complex at membrane-aqueous interface and permeates through the membrane phase [2]. At the membrane-aqueous interface, complex release the carrier at the membrane phase due to certain chemical reaction. Therefore, concentration of the solute at the membrane-aqueous interface is maintained at zero that allows a continuous driving force for the solute permeation through the membrane phase.

In this study, a general model was developed to predict the performance of ELM on the kraft lignin removal. The model was developed by using MATLAB software, and the mathematical equation was solved using built-in function of MATLAB known as ode45. Three parameters include treat ratio, carrier concentration, and initial concentration of solute at external phase were investigated in this study in order to determine the optimum operating condition of ELM.

2.0 EXPERIMENTAL

In order to study the performance of ELM system on the kraft lignin removal, a mathematical model is developed by using MATLAB software. This model is developed based on the assumptions as following:

i. Feed phase is well-mixed.
ii. Process is isothermal at perfect mixing and all physical properties remain throughout the process.
iii. No loss of complex and carrier.
iv. Carrier concentration is constantly consumed on the outer interface of the membrane and reformed on the inner interface.
v. Internal droplets are immobilized due to presence of surfactant and uniformly distributed inside emulsion globules.

The mathematical model developed was based on the research of Biscaia *et al*. [9]. Biscaia's model was found to be numerically stable and reliable in predicting the behavior of solute extraction using emulsion liquid membrane for a long time periods. In this finding, kraft lignin (A) was removed from external phase by reacting with carrier (B) and formed complex (C) that can enter the membrane phase as shown in reaction (1) whereby H^+ released determined the value of pH:

Reaction between carrier (B) and solute (A):

$$A^- + B^+ \longrightarrow BA + H^+ \quad (1)$$

The complex (C) was then reacted with stripping reagent in order to strip the solute into the internal phase. The BH formed will be a carrier at external phase again. The reaction of the complex and stripping agent is as shown in reaction (2).

Reaction of the complex (C) and stripping agent (H):

$$BA + H^+ \longrightarrow BH + A^+ \quad (2)$$

The swelling occurred during which the radius of the emulsion liquid membrane was expanding. The rate of change of the radius depends on the concentration of solute, membrane, stripping agent and carrier of in the system. Equation (3) displays the formula for change of radius.

$$\frac{dR}{dt} = P_0 V_{H_2O}\{g_1[2\overline{C_{A1}}(t) + \overline{C_{H1}}(t) + \overline{C_C}(t)] - g_2[2\overline{C_{A3}}(t) + \overline{C_{H3}} + \overline{2C_B}] \quad (3)$$

where P_0 (m/s) is the mass transfer coefficient of water that can be calculated by the simplest mass transfer theory as shown in Equation (4). V_{H20} (m^3/kmol) is the partial molar volume of water.

$$P_0 = \frac{D_e}{\delta}(C_{A30} - C_{A3}) \quad (4)$$

In this finding, the transient superficial area of N spherical (W/O/W) emulsion globules is the function of the radius of the globule, where the volume of the internal phase changed with swelling and breakage rate of the droplets, as shown in Equation 5.

$$NS(t) = 4\pi NR^2(t) = 3\frac{V_1(t)+V_2}{R(t)} = 3\left(\frac{V^0{}_1+V_2}{R(t)}\right)R^3(t) \quad (5)$$

In this finding, the mass balance of the solute at external phase and internal phase was highlighted in order to determine the performance of the ELM in removing kraft lignin. Equation (6) and (7) show the mass balance of solute at external phase and internal phase respectively.

$$\frac{dC_{A3}}{dt} = \frac{-3D_e}{R(t)}(V_2 + V_3)x\,\frac{k_f}{D_e}(C_{A3} + C_{A3}{}^*) \quad (6)$$

$$\frac{dC_{A1}}{dt} = \frac{S'(t)}{V_1(t)}r_s - \frac{C_{A1}(t)}{V_1(t)}\frac{dV_1(t)}{dt} - k_b C_{A1}(t)|_{r=R} \quad (7)$$

Where the C_{A3*} is the interface concentration of solute which can be calculated using Equation from (8) to (10).

$$C^*{}_{A3}(t) = C^0{}_{A3}\left[\frac{3}{Z+3} + S(t)\right] \quad (8)$$

$$S(t) = \frac{2(Z - Zb^2(t))exp(-b^2(t)T/\omega)}{3Z + Z^2 + b^2(t) + Gb^2(t)x\,(Gb^2(t) - 2Z - 1)} \quad (9)$$

$$\tan b(t) = \frac{b(t)[Z - (Gb(t))^2]}{Z + b^2(t)(1-G)} \quad (10)$$

Where the value of Z,w,G,T(t) and f can be obtained from equation (11) to (15).

$$Z = m\omega f \quad (11)$$

$$\omega = 1 - \phi_1 + \phi_1 q \quad (12)$$

$$G = \frac{mD_e}{Rk_f} \quad (13)$$

$$T(t) = \frac{D_e t}{R^2} \quad (14)$$

$$f = \frac{3\phi_2}{1-\phi_2} \quad (15)$$

Mass balance of carrier (B) and complex (C) is shown in equation (16) and (17) respectively.

$$\frac{dC_B}{dt} = \frac{1}{1-\phi_1}\frac{\delta}{\delta r}\left[r^2\frac{\delta C_{B\,(r,t)}}{\delta t}\right] + \frac{3\phi_1}{R_\mu}r_s \quad (16)$$

$$\frac{dC_c}{dt} = \frac{V_1(t)+V_2}{V_2}\frac{D_e}{r^2}\frac{\delta}{\delta r}\left[r^2\frac{\delta C_{c\,(r,t)}}{\delta t}\right] - \frac{S'(t)}{V_2}r_s \quad (17)$$

The data used for the simulation program is based on the experimental data from Othman *et al*. [8] regarding the extraction of silver using emulsion liquid membrane. The data applied into the MATLAB is shown in Table 1.

Table 1 Data for MATLAB software

Experimental Parameter	Value
Treat ratio	1:5
Initial concentration of solute at external phase, C_{A3}^0	4600ppm
Initial concentration of solute at internal phase, C_{A1}^0	0ppm
Initial concentration of stripper at internal phase, C_{H1}^0	1.0M
Initial concentration of carrier, C_B^0	0.05M
Radius of emulsion droplets, Rμ	2.74 X 10^{-6}m
Volume fraction internal in emulsion drop	1:1
Equilibrium Constant and Relative Diffusivities	
k_c	0.0022m/s
D_e	$2.312x10^{-9}m^2/s$
k_s	$1.5x10^{-8}m^4$/mol.s
R	5 X 10^{-4}m

■3.0 RESULTS AND DISCUSSION

3.1 Validity of the Model using MATLAB software

The result obtained via MATLAB programming was compared with the model from Lin and Long to determine the validity of the model [9]. Figure 1 describes that the solute at the feed phase was extracted rapidly into the internal phase at the first 3 min and becomes stable after 5 min Kraft lignin was extracted rapidly at the beginning of the extraction process because it was a fast reaction process. The solute reacted with the carrier and was extracted into the membrane phase and soon stripped into internal phase. The result shown in Figure 1 is compatible with the theory of emulsion liquid membrane applied by Lin and Long as shown in Figure 2 [9].

The efficiency of the system was different as both of the models are applied on different types of solutes. However, by comparing Figure 1 and 2, the behaviour of both graphs are similar where the extraction process is rapid at the initial part of the reaction and become slower after some time. Thus, the result of MATLAB software is acceptable after comparing with the result from previous published paper.

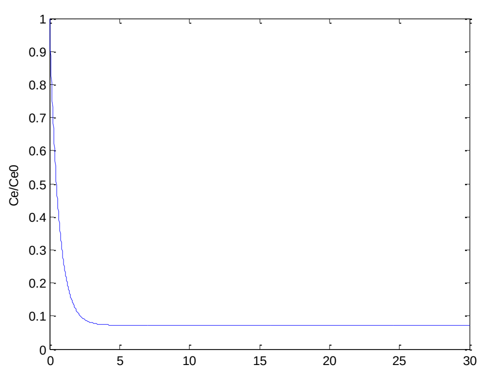


Figure 1 Concentration of solute at external phase for 30mins. [Condition: Concentration of feed phase = 4600ppm, carrier concentration = 0.3M, treat ratio = 0.2, pH = 3.6]

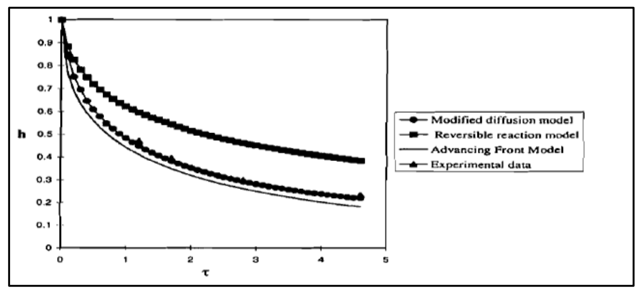


Figure 2 Results of different modeling on emulsion liquid membrane (Lin and Long, 2010)

3.2 Effect of Treat Ratio

Treat ratio is defined as the volume ratio of the emulsion to the feed phase. The results of the four different values of treat ratio were obtained through MATLAB software. Figure 3 shows the trend of the graph for four different values of treat ratio of 0.05, 0.1, 0.2 and 0.5. From Figure 3, it can be noticed that treat ratio of 0.5, 0.2, 0.1 and 0.05 extracted 93.49%, 84.74%, 72.29% and 53.07% respectively. The highest extraction efficiency was at 0.5 treat ratio, where 93% of solute was extracted within 6 min.

High treat ratio which represents bigger volume of stripping phase will increase the mass transfer resistance and hence longer time is required to extract out the solute from the feed phase. For the ELM system, the longer extraction time will lead to the breakage phenomenon. The performance of the emulsion liquid membrane was determined according to the time extraction and also the percentage of the solute extracted. Thus, the treat ratio of 0.2 was selected as the optimum treat ratio to extract the solute as it can extract high percentage of solute within 120s.

The result obtained is comprised with the published journal. From the study by Othman *et al.* [8], the extraction efficiency is decreased due the increase of the volume of external phase. Low treat ratio will cause low extraction efficiency because it lacks internal reagent in the droplets to react with solute transported through the liquid membrane. Thus, solute is accumulated in the membrane and thus results in the lack of carrier to diffuse back to react with solute in feed phase. Masu *et al.,* stated that the volume ratio does not affect much on stability of the membrane as the increasing of the treat ratio is only decreased the breakage very slightly [10].

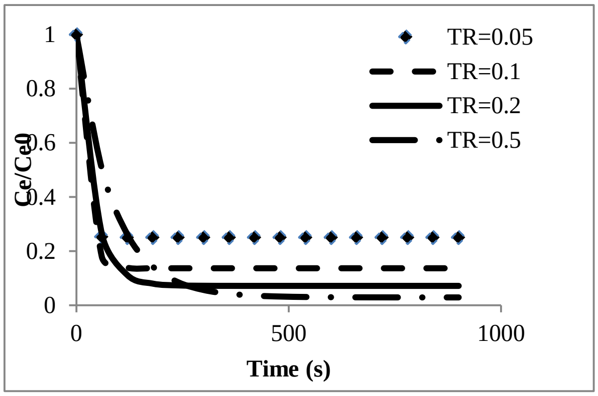


Figure 3 Varies treat ratio on effect of kraft lignin extraction. [Condition: Concentration of feed phase = 4600ppm, Carrier concentration = 0.3M, pH = 3.6]

3.3 Effect of Carrier Concentration

Figure 4 shows that the increasing of the carrier concentration leads to increase of solute extraction. The results show that within 200s 97.34%, 92.81%, 37.25%, 53.06% and 84.74% of solute was extracted using 0.5M, 0.3M, 0.08M, 0.1M and 0.2M carrier, respectively.

The range of the carrier concentration was simulated based on the ongoing experiment. Figure 4 shows that the high carrier concentration extracts more concentration of solute from external phase. This is due to increase of carrier concentration provides a greater driving force for solute to transfer into internal phase from external which can be proved by Das *et al.* [11]. From the results obtained, 0.3M and 0.5M extract out similar amounts of solute from external phase but 0.3M is selected as the optimum carrier concentration for the ELM system as the higher carrier concentration will cause the swelling effect in experiment.

Das *et al.* mentioned that high concentration of carrier in membrane phase will increase the viscosity of the membrane phase and form small globules of emulsion [11]. Thus, the mass transfer of solute between feed phase and internal phase also increases because the small globules results in larger surface area. From the data obtained, the carrier concentration of 0.3M and 0.5M can extract out the similar amounts of kraft lignin due to two reasons, as explained by Othman *et al.* [8]. Firstly, there is a maximum percentage of unstripped solute in the membrane phase, which then affects the solute extracted by ELM system. The second reason is that the swelling of the emulsion increased with the increasing of carrier concentration and leads to dilution of internal phase.

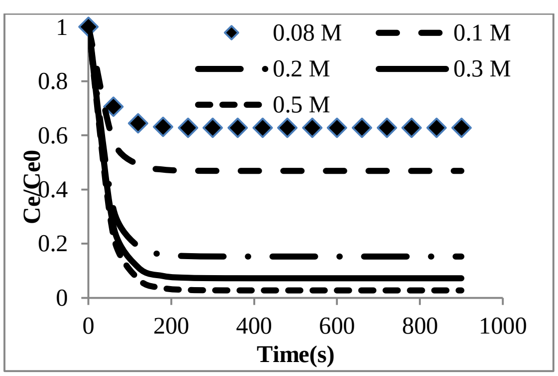


Figure 4 Varies carrier concentration on effect of kraft lignin extraction. [Condition: Concentration of feed phase = 4600ppm, treat ratio = 0.2, pH = 3.6]

3.4 Effect of Concentration of Aqueous Feed Phase

Figure 5 shows the effect of initial concentration of feed phase towards the performance of ELM system on the recovery of kraft lignin. The findings revealed that the higher concentration at external phase exhibited the lower extraction efficiency. From Figure 5, initial concentration of external phase at 0.5g/L, 4.6g/L, 15g/L, 40g/L extract out 93.36%, 92.81%, 97.65% and 92.52% of solute from external phase, respectively. The range of the parameters used in the model was from 0.5g/L to 40g/L as existing concentration of kraft lignin from pulping wastewater was around 40g/L. Thus, the optimum initial concentration of external phase was determined to ease the experimental work in diluting the solute.

From Figure 5, it can be noticed that 15g/L of external phase extracted the most amount of solute from feed phase within 600s of extraction time. Figure 5 also describes that higher initial concentration of external phase requires longer time to extract solute from the aqueous feed phase. For example, 40g/L of external phase cannot archieve the maximum percentage of extraction within 15mins. This is because the swelling effect is increased with the feed phase hence increasing in mass transfer resistance, which then prolongs the extraction time. For this parameter, the optimum initial concentration of solute at external phase is 500ppm, which can extract high percentage of solute with the shortest extraction time. The results obtained were similar to previous work performed by Othman *et al.*[12].

Increasing in concentration of external phase will reduce the performance of the solute removal by ELM system. This is because the complex will diffuse into the inner region of the globules to release the solute in the stripping phase at the high concentration of solute. Besides that, the swelling effect is also increased with the increasing concentration in the external phase due to the osmotic pressure between the external and internal phase.

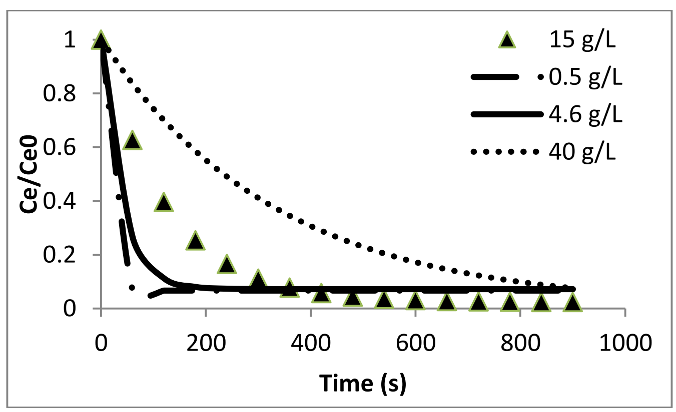


Figure 5 Effect of initial concentration of kraft lignin at external phase on extraction performance. [Condition: Carrier concentration = 0.3M, treat ratio = 0.2, pH = 3.6]

4.0 CONCLUSION

In conclusion, the model developed shows that the concentration of the solute at the internal phase increases gradually initially, and become stable after some time. The result obtained from the model is typically similar with the trend of the model developed by others such as Lin and Long. Therefore, the model can be applied for kraft lignin removal with emulsion liquid membrane system. Results also revealed that the percentage of solute extracted increased with increasing treat ratio and carrier concentration, however it decreased when the initial concentration of external phase is increased.

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