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Prediction of Zinc Extraction using Facilitated Emulsion Liquid Membrane Model

Norul Fatiha Mohamed Noah[a,b], Norasikin Othman[a,b,*], Hakim Binanga[a]

[a] School of Chemical & Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia; [b] Centre of Lipids Engineering and Applied Research (CLEAR), Ibnu Sina Institute for Scientific and Industrial Research (ISI-SIR), Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

Abstract   This study presents the modelling of zinc extraction facilitated by emulsion liquid membrane (ELM). The previous model by Ooi (2015) was extended and modified in accordance with the present research objectives and scope for prediction of Zinc extraction. The modified model is based on the chemical interaction between the carrier molecules and zinc ions, as well as the mass transport mechanism. Furthermore, the model also accounts for the effect of Sauter mean diameter of the emulsion on the extraction efficiency. MATLAB was applied to simulate the ELM extraction of zinc-based on the validated model. The model was validate using experimental data by Reis and Carvalho (2004). The simulation result showed an agreement with experiment data where 100% of Zn was extracted at optimum condition of 1:6.15 treat ratio, 300ppm of initial zinc concentration, 8 w/v % of (bis(2-ethylhexyl)thiophosphoric acid (D2EHTPA) as carrier, and 2.5 M sulphuric acid (H_2SO_4) as stripping agent. The consistent results between the experimental and simulated data increased the reliability of the model as a viable prediction tool for zinc extraction using facilitated ELM.

Keywords: Membranes, Emulsion, Zinc extraction, Modelling, Sauter mean diameter.

Introduction

Rapid industrialisation in the 21st century has led to the omnipresent existence of heavy metals in the environment, especially zinc. Zinc in industrial effluent is commonly found in the inorganic form in +2 oxidation state. Zinc is an essential element in various industrial processes, such as the electroplating industry, metallurgical operational units, and the mining industry [1]. However, excessive use of zinc and other heavy metals in industrial processes can cause severe harm to the environment and detrimental effects on human health due to their toxic characteristics [2]. Therefore, the development of a suitable and effective method of zinc extraction is of major interest due to its economic value and environmental concerns.

Various methods have been commercially used for the extraction of heavy metals in industrial effluent. These methods are activated carbon [3], chemical precipitation [4], and ion exchange [5]. Chemical precipitation is one of the most commonly used methods for the extraction of heavy metals. However, this method lacks qualities, such as producing an excessive amount of sludge, high chemical consumption, and inability to extract low concentrations of heavy metals [6]. Therefore, the need to develop a more feasible and efficient method of heavy metal extraction arises. The emulsion liquid membrane (ELM) technology has emerged as a viable approach for heavy metal separation since its invention by Li [7]. This is due to the advantages of the ELM process, such as high interfacial area,

selective, and requires a small amount of organic solvent [8][9]. Furthermore, the ELM process has been investigated for the extraction of metal ions, such as copper [10], zinc [11], nickel [12][13], silver [14], and chromium [15].

Emulsion liquid membrane is a three-phase emulsion system, typically water-in-oil-in-water (W/O/W). This system contains a homogeneous thin film of organic liquid, which serves as a barrier between two aqueous phases of different compositions. The ELM technology could be described as a "bubble within a bubble." The outer bubble contains the extractants or carriers, whereas the inner bubble contains the internal phase reagent. Anything surrounding the bubble is known as the external or continuous phase. Although the effectiveness of ELM has been demonstrated for several heavy metal extraction processes, this method suffers from emulsion instability. In general, emulsion instability involves emulsion swelling, coalescence, and membrane leakage. The unstable emulsion will affect the extraction efficiency. However, highly stable emulsion can cause difficulty during settling and demulsification [16]. Therefore, to overcome the ELM instability, its formulation such as treat ratio, initial zinc concentration, carrier concentration, and stripping agent concentration is crucial.

In addition, mathematical models serve as a major role to improve the understanding of the process and to optimize the process operating conditions in order to achieve the maximum efficiency of the process. A variety of studies and research have been done for the development and examination of mathematical modelling for the mass transfer of solute through liquid membranes include modeling of transport of nickel(II) [12], modelling of zinc extraction from sulphate solutions with bis(2-ethylhexyl)thiophosphoric acid [11] and. kraft lignin extraction [20]. Suliman et al., [28] have developed correlation of sauter mean diameter. The present paper aims to simulate and validate zinc extraction using facilitated ELM by modifying the previous model to obtain a more reliable result. This modification includes the incorporation of the Sauter mean diameter predictive model.

Materials and Methods

Droplet Size Prediction Model
The theory of Hinze-Kolmogorov was employed to develop the Sauter mean diameter correlation in the stirrer vessel. This method was also used by various authors, such as Angle and Hamza [17], Raji et al. [18], and Toschi et al. [19]. The modification of the Hinze-Kolmogorov model gives the general form in Equation (1) for the prediction of droplet size:

$$\frac{d_{32}}{D} = 0.081(1 + 4.47\phi)We^{-0.6} \tag{1}$$

The $(1+4.47\phi)$ term indicates the effect of the dispersed phase volume fraction ϕ that reflects the system turbulence. The term 0.081 is a constant and 4.47 is the coefficient specific to the liquid-liquid system. We is the Weber number, which is dimensionless and usually used to scale up at geometric similarity. The We is defined by Equation (2):

$$We = \frac{\rho_c N^2 D^3}{\sigma} \tag{2}$$

Where ρ_C is the density of the feed phase, N is the impeller speed, D is the impeller diameter, and σ is the interfacial tension.

Extraction Mechanism of Zinc
Metal transfer through a liquid membrane is an example of a carrier-facilitated transport model. Generally, the metal ion is extracted from the aqueous feed phase through a chemical reaction with the extractant at the external-membrane interface and stripped out by the reverse reaction at the surface of the internal droplets. Meanwhile, the regenerated extractant returns to the external process to restart the process. Figure 1 shows the schematic representation of the liquid membrane globule

concentration profile of zinc through ELM.

The zinc extraction by incorporating an extractant follows the following reaction, as shown in Equation (3) and simplified to Equation (4):
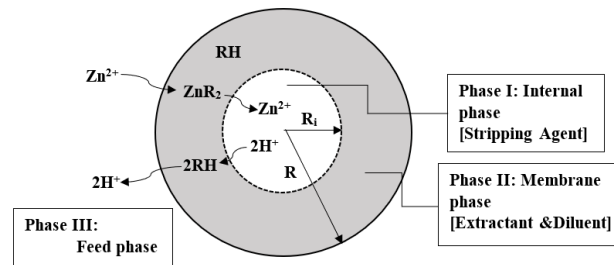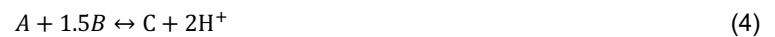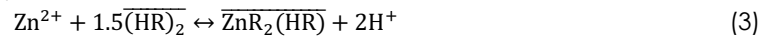
$$Zn^{2+} + 1.5\overline{(HR)_2} \leftrightarrow \overline{ZnR_2(HR)} + 2H^+ \tag{3}$$

$$A + 1.5B \leftrightarrow C + 2H^+ \tag{4}$$

Figure 1 A schematic representation of liquid membrane globule concentration profile of zinc through ELM.

The extraction performance of the ELM was measured using Equation (5):

$$E = \frac{C_{A30} - C_{A3}}{C_{A30}} \tag{5}$$

Emulsion Liquid Membrane Modelling

The proposed model for the extraction of zinc using the facilitated ELM model in this research is based on the model proposed by Ooi et al. [20], which is a further development of the model proposed by Yan et al. [21] and Biscaia Junior et al. [22]. In order to obtain a reliable mathematical model of ELM that is valid for long periods, the emulsion breakage and swelling were considered and the model was developed based on the following assumptions:

   i. The size distribution for internal droplets and globules is uniform and can be expressed as the Sauter mean diameter.
  ii. There is no internal circulation inside the emulsion globules due to the adequate amount of surfactants that immobilise the internal aqueous phase droplets.
 iii. Coalescence and redistribution of the emulsion globules are negligible.
  iv. The local reaction equilibrium applies throughout the globules as the chemical reaction rate is faster than the diffusion within the globules.
   v. Distribution coefficient at the internal-membrane interface is equal to the external-membrane interface.
  vi. The external phase is mixed thoroughly. The mass transfer resistance in the external phase is restricted to the external boundary layer surrounding the globules.
 vii. Due to the small size of the droplets, the internal mass transfer resistance is negligible.
viii. At perfect mixing, the process is isothermal; thus, the physical properties are constant during the extraction.
  ix. The pH of the external aqueous phase remains constant throughout the process.

The extraction by diffusion and non-facilitated transport of the solute without the extractant are negligible.

Although emulsion breakage and swelling are considered, the number of emulsion globules remains constant. This is based on the assumption that emulsion breakage occurs at the outermost droplets in the globules.

Zinc Extraction Model Formulation

Based on the mass balance in Equation (6) and assumptions from Section 2.3, the governing equations for the model prediction in the ELM process are:

Mass balance of the solute in the external phase.

$$V_3 \frac{dC_{A3}}{dt} = -k_{OC} \frac{3(V_1 + V_2)}{R}(C_{A3} - C_{A3}^*) + k_B C_{A1} V_1 \tag{6}$$

Where C_{A3} is the Zn^{2+} concentration in the external phase (mg/L), C_{A3}^* is the Zn^{2+} concentration in the external-membrane interface (mg/L), and k_{OC} is the external phase mass transfer coefficient.

Mass transfer fluxes at the external-membrane interface.

The mass transfer flux outside and inside the external-membrane interface is equal due to no solute accumulation at the external membrane interface, as shown in Equation (7). The driving force at the external film resistance is the concentration gradient between C_{A3} and C_{A3}^*.

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

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

Where N represents the total number of emulsion globules, R is the emulsion globule radius, D_{eC} is the effective diffusivity of the complex in the emulsion phase (m^2/s), C_c is the complex concentration at the external-membrane interface (mg/L), $D_{eC}\left(\frac{\partial C_C}{\partial r}\right)_{r=R}$ is the diffusion mass transfer flux inside the external-membrane interface, $k_{OC}(C_{A3} - C_{A3}^*)$ is the mass transfer flux outside the external-membrane interface, and m is the distribution coefficient of the extraction.

Mass transfer of carrier and complex inside the emulsion globules (0 ≤ r ≤ Ri).

The effective diffusivities of the complex and carrier, D_{eC} and D_{eB} (m^2/s) were employed to express the mass balance equations of the carrier B and the complex C inside the emulsion globules, as shown in Equation (8) and (9), respectively:

$$\frac{\partial C_C}{\partial t} = \frac{(V_1 + V_2)}{V_2}D_{eC}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_C}{\partial r}\right)\right) - \frac{S'r_s}{V_2} \tag{8}$$

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

Where V_1 and V_2 are the internal and membrane phase volume (mL), respectively, $(V_1 + V_2)$ is the emulsion total volume (mL), C_B and C_C are the carrier and complex concentrations at the external-membrane interface (mg/L), respectively, r_s is the stripping rate, and S' is the interfacial area between the internal droplets and the membrane phase (m^2).

Mass balance of Zn^{2+} and stripping agent in the internal phase.

The mass balance equations of the solute A and the stripping agent S in the internal phase are shown by Equation (10) and (11), respectively:

$$V_1 \frac{dC_{A1}}{dt} = S'r_s - C_{A1}\frac{dV_1}{dt} - k_b C_{A1} \tag{10}$$

$$V_1 \frac{\partial C_{S1}}{\partial t} = -\frac{3V_1}{R_{m\mu}} r_s \tag{11}$$

Equilibrium: $C_{A1} = qC_C$

Where V_1 is the internal phase volume (mL), C_{A1} is the Zn^{2+} concentration in the internal phase (mg/L), k_b is the breakage rate (min^{-1}), C_{S1} is the stripping agent concentration in the internal phase (mg/L), $R_{m\mu}$ is the emulsion droplet radius (m), and q is the stripping distribution coefficient.

Emulsion swelling.

Swelling occurred during the expansion of emulsion globules. The rate of radius change depends on the concentration of the membrane, solute, carrier, and stripping agent. Equation (12) presents the formula for the radius difference. Meanwhile, the internal phase transient volume is shown in Equation (13):

$$\frac{dR}{dt} = k_{OC} V_{H_2O} [g_1(C_{A1} + C_{S1}) - g_3(C_{A3} + C_{S3})] \tag{12}$$

$$\frac{dV_1}{dt} = 4\pi R^2 k_{OC} V_{H_2O} [g_1(C_{A1} + C_{S1}) - g_3(C_{A3} + C_{S3})] \tag{13}$$

Where k_{OC} is the mass transfer coefficient at the external phase (m/s), V_{H_2O} is the partial molar volume of water (m^3/kmol), and g is the osmotic coefficient.

The numerical method was used to transform the non-linear partial differential equations (PDEs) into ordinary differential equations (ODEs). After that, the ODEs were solved by using MATLAB software built-in ode45 function.

Modelling Parameters

The parameters required in this model were divided into three categories: chemical and physical properties, operating conditions, and diffusivity and mass transfer coefficients. Several parameters can be calculated through specific equations, including the mass transfer coefficient, effective diffusivity, equilibrium constant, globule diameter, distribution coefficient, as well as forward and backward extraction constant. Several parameters shown in this present study are based on previous research by Reis and Carvalho [11] and Ooi [20]. The typical values for each parameter are listed in Table 1.

Experimental Data

In order to simulate and validate the developed model, the previous experimental data reported by Reis and Carvalho [11] were used. In the experiment, the emulsion was produced by mixing 20 mL of aqueous internal phase containing a stripping agent (H$_2$SO$_4$) with 110 mL of organic membrane phase. The organic membrane phase contained a diluent (Shellsol T, Shell Chemical Ltd.), a surfactant (Polyamine ECA4360J, Essochem Europe Inc.), and a carrier (bis(2-ethylhexyl)thiophosphoric acid (D2EHTPA), Höchst AG.). The emulsion was dispersed in 800 mL of external aqueous phase containing zinc in a glass reactor with two stainless steel baffles. The W/O/W dispersion was stirred with a stainless steel paddle with a diameter of 4.5 cm at 4.67 rps. Table 2 shows the overall summary of the experimental conditions.

Results and Discussion

Validation of the Droplet Size Prediction Model

To obtain the validity of the droplet size prediction model, the predicted Sauter mean droplet diameter was compared with the result attained from previous experiments [11]. The average absolute relative error (%AARE) was used to quantitatively measure the reliability of the predictive model. The comparison between the d$_{32}$ predictive model and the experimental results at different stirring speeds

is illustrated in Figure 2.

Table 1 Modelling parameter [11] [23]

Parameters	Value
Initial volume of internal phase, V_1^0	20 mL
Volume of internal phase, V_1	20 mL
Volume of membrane phase, V_2	110 mL
Treat ratio TR	0.1615 (1:6.15)
Initial Zn^{2+} concentration in external phase, C_{A3}^0	300 mg/L
Initial Zn^{2+} concentration in internal phase, C_{A1}^0	0 mg/L
Initial stripping agent concentration in internal phase, C_{S1}^0	2.5M
Initial carrier concentration, C_B^0	0.09M
Effective diffusivity of complex in membrane, D_{e_C}	1.602×10^{-8} m²/min
Mass transfer coefficient, k_{OC}	4.02×10^{-3} m/min
Breakage rate, k_b	1×10^{-5}/min
Volume ratio of internal phase to emulsion drop, ϕ_1	0.1538
Volume ratio of emulsion to total volume of phase, ϕ_2	0.1398
Radius of emulsion droplets, $R_{m\mu}$	1×10^{-6} m
Radius of emulsion globules, R	4.5×10^{-4} m
External distribution coefficient, m	97.96
Stripping distribution coefficient, q	0.98
Rate of Extraction, re	23.73 mg/L min
Rate of Stripping, rs	23.73 mg/L min
Equilibrium Constant, Keq	239.9

Table 2 Overall summary of the experimental conditions [11].

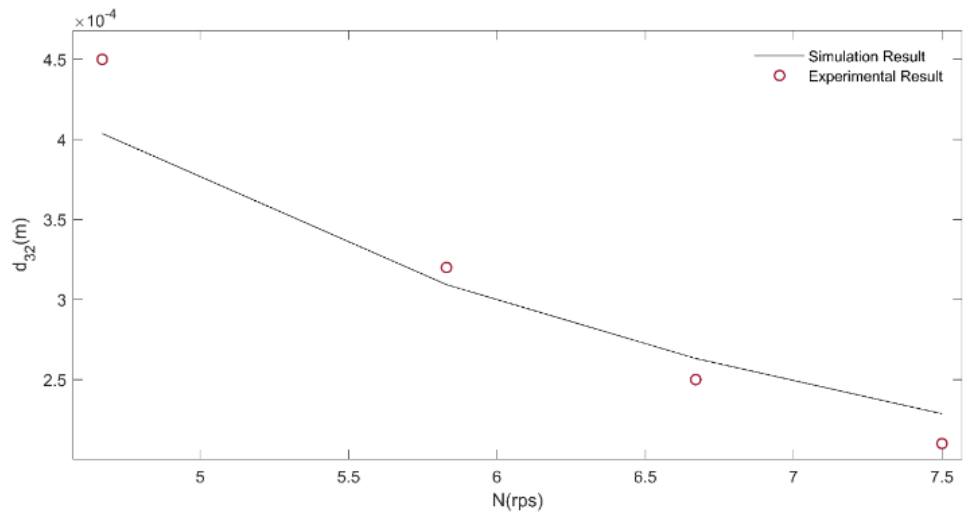| Chemicals Used	
External phase	$ZnSO_4$
Stripping agent	H_2SO_4
Carrier	bis(2-ethylhexyl)thiophosphoric acid (D2EHTPA), Höchst AG.
Surfactant	Polyamine ECA4360J, Essochem Europe Inc.
Solvent	Shellsol T, Shell Chemical Ltd.
Equipment Used	
Reactor	Glass reactor (85 mm ID, 1 L) with two stainless steel baffle (205 mm×7 mm×5 mm) with a gap of 5 mm with the wall
Impeller	Stainless steel paddle (45 mm×45 mm×5 mm)
Base Operating Conditions	
Impeller speed	4.67 rps
Surfactant	2 w/v%
V(I)	20 mL
V(II)	110 mL
V(III)	800 mL
Treat ratio	1:6.15 to 1:15
D2EHTPA	5 - 8 w/v%
Zn (III)	300 -1000 mg/L
H_2SO_4(I)	1.5 - 2.5 M

Figure 2 Validity of the d_{32} prediction model.

The predictive model obtained has relatively similar results with the experimental data, with an AARE value of 6.9%. This finding shows that the correlations in the present work are consistent with the experimental data. It is believed that the swelling and emulsion breakage resulted in the deviation of the globule size. Basically, the size of emulsion depends on the We value, which is related to stirring speed. The distribution of the Sauter mean diameter of the emulsion globules at various stirring speeds is shown in Figure 3.
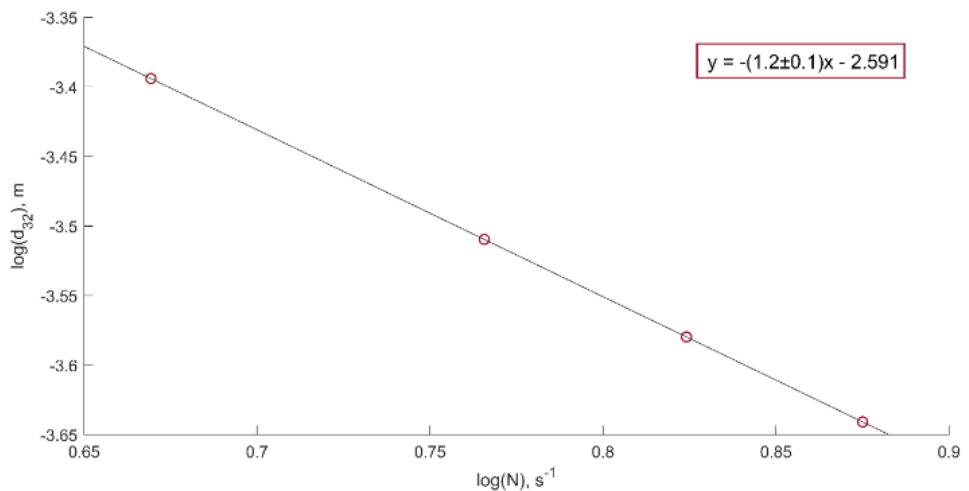

$$y = -(1.2 \pm 0.1)x - 2.591$$

Figure 3 Effect of stirring speed on the Sauter mean diameter of the emulsion globules (d_{32} data points are obtained from the predictive model, N = 4.67–7.50 rps).

The findings suggest that the size of the emulsion globules is proportional to N-1.2, which further supports the idea of various authors [16, 24]. It can be deducted that the d_{32} is inversely correlated with stirring speed. This implies that the increase in stirring speed resulted in greater turbulence and collision energy, leading to the formation of smaller droplet size. A similar result was also reported by Raji et al. [18]. The turbulent environment prevents the coalescence between emulsion globules and increases the occurrence of emulsion globules to collide with internal walls, which in turn decreases the globule size. Consequently, the globule breakage dominates their coalescence.

Validation of the Model

A comparative study between the experimental and simulation data results at the optimum conditions was conducted to evaluate the validity of the predictive model. The experimental results were obtained from the previous work by Reis and Carvalho [11]. These results show the reliability of the model for zinc extraction using facilitated ELM, expressed in C_{A3}/C_{A30} vs time. Figure 4 presents the validity of the model.

The simulation results suggest that zinc was fully extracted from the external phase at 6 min. However, the experimental result shows a slight difference, with the extraction efficiency of 97% at 6 min. Furthermore, a slower reaction rate was also observed in the experimental results. The standard mean deviation in the experimental results relative to the simulated ones in the present work was 6.15%. This result indicates that the simulated data are in good agreement with the experimental data in the extraction of zinc using ELM. A similar result for the standard mean deviation of the model was also reported by Reis and Carvalho [11]. The deviation of the model from the experimental data is likely to be related to the non-ideal phenomena that appeared during the experiment.

Furthermore, the slight differences may also be due to errors in estimating the model parameters. The consistency of the experimental data and simulated results promotes confidence as a viable predictive model for the parametric study in the ELM process.
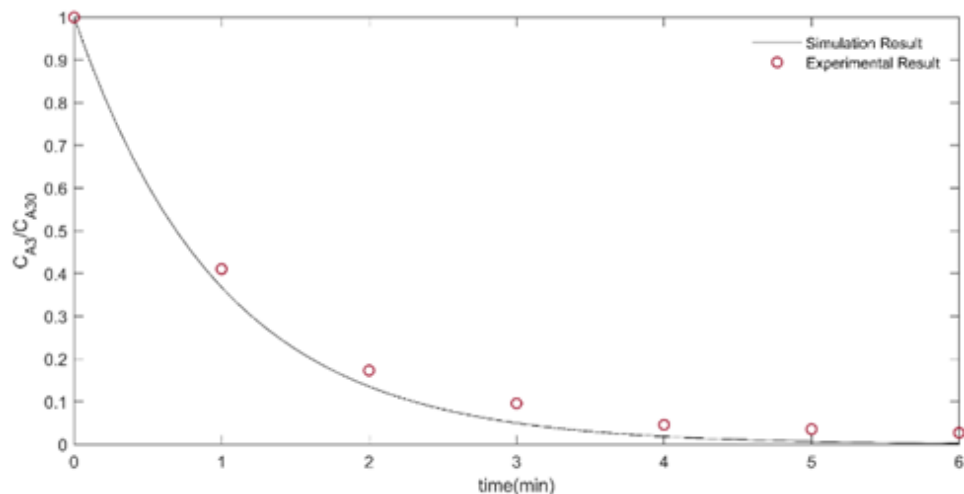

Figure 4 Comparison between experimental data and model prediction (Experimental conditions: [Zn (III)] = 300 mg/L; [H_2SO_4 (I)] = 2.5M; [D2EHTPA] = 5 w/v%).

Parametric Study of the ELM Model

Effect of Treat Ratio

The treat ratio in the ELM process represents the volume ratio of the emulsion to the external phase. The treat ratio value is crucial to ensure an adequate amount of stripping agent in the internal phase for the reaction with solute from the external phase, which is Zn^{2+}. The influence of treat ratio in the range of 1:6.15–1:15 on the extraction of zinc is illustrated in Figure 5.

The simulation suggests that increasing the treat ratio will generally lead to a better extraction rate and extraction efficiency. At the treat ratio 1:6.15, the extraction efficiency reached 99.75%. On the other hand, lower treat ratios at 1:10 and 1:15 only reached an extraction efficiency of 95.31% and 91.86%, respectively. This is due to the increase in the emulsion volume at a higher treat ratio, which corresponds to the increase of the carrier, stripping agent amount, and also the overall mass transfer area. Furthermore, the increment of treat ratio is generally attributed to a larger size of emulsion globules due to the increase of hold-up emulsion volume. Subsequently, the interfacial area between

the membrane phase and the external phase increases, leading to an increased extraction rate. This finding is supported by Fouad and Bart [25]. From the industrial perspective, the amount of emulsion used must be determined precisely to obtain the optimum value between extraction efficiency and cost efficiency to ensure that the process is economically viable.
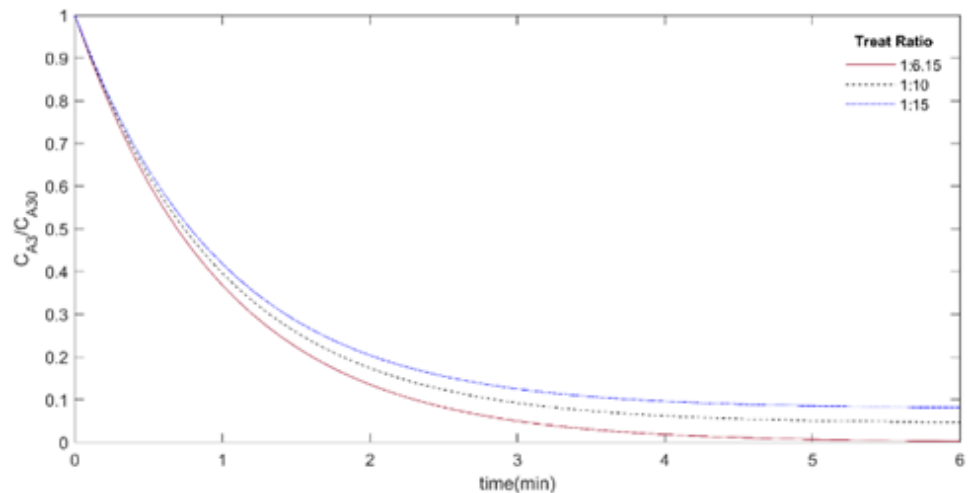

Figure 5 Effect of treat ratio on zinc extraction by model prediction.

Effect of Initial Zinc Concentration in the External Phase

The main driving force for the extraction process in an ELM system is the concentration gradient of the solute at the external phase and the internal phase. The initial zinc concentration in the external phase was varied from 300 to 1,000 mg/L, and the result is illustrated in Figure 6. The simulation results show that extraction efficiency is influenced by the initial zinc concentration in the external phase. In general, the extraction performance decreases with zinc concentration. The extraction efficiency values at 6 min for the concentrations of 300, 500, and 1,000 mg/L were 99.75%, 92.78%, and 80.89% respectively. At a lower zinc concentration, almost all the extracted zinc in the ELM will be stripped and confined in the internal phase. However, at a higher zinc concentration, most of the extracted zinc will retain in the membrane phase. This situation is due to the zinc-carrier complexes that must diffuse into the deeper region of emulsion globules for the zinc to be released in the internal phase. This phenomenon is caused by the increase of the diffusional path through the emulsion globules as the internal phase at the peripheral region saturates faster at a higher zinc concentration. It can be inferred that the resistance of mass transfer in the emulsion globules plays an important role. This finding broadly supports the work of other studies linking the performance of extraction with the initial external phase concentration [10, 23]. Therefore, more stripping agent is required to compensate for the increase of the initial zinc concentration to achieve better extraction efficiency.

Effect of Carrier Concentration

In the ELM process, the carrier that chemically reacts with the solute at the external-membrane interface is vital to produce carrier-solute complexes. The carrier must be capable of acting as a shuttle to selectively transport the solute through the membrane phase and into the internal phase. Figure 7 exhibits the effect of carrier concentration (5–8 w/v%) on the behaviour of zinc extraction.

The result shows that a further increase in D2EHTPA concentration from 5 to 8 w/v% increased the extraction efficiency from 94.63% to 99.75%, respectively. This outcome suggests that more Zn-D2EHTPA complexes were formed, resulting in an increase in the transportation of zinc from the external phase to the internal phase. This result agrees with Kulkarni and Mahajani [26], who reported that the increase in the carrier concentration led to a higher degree of solute extraction. However, it is

believed that a very high amount of carrier in the membrane is not beneficial due to the increase in viscosity, which in turn will increase the diameter of the globules. Furthermore, the increase of carrier concentration also promotes emulsion swelling, which dilutes the aqueous receiving phase and decreases the efficiency of the process.
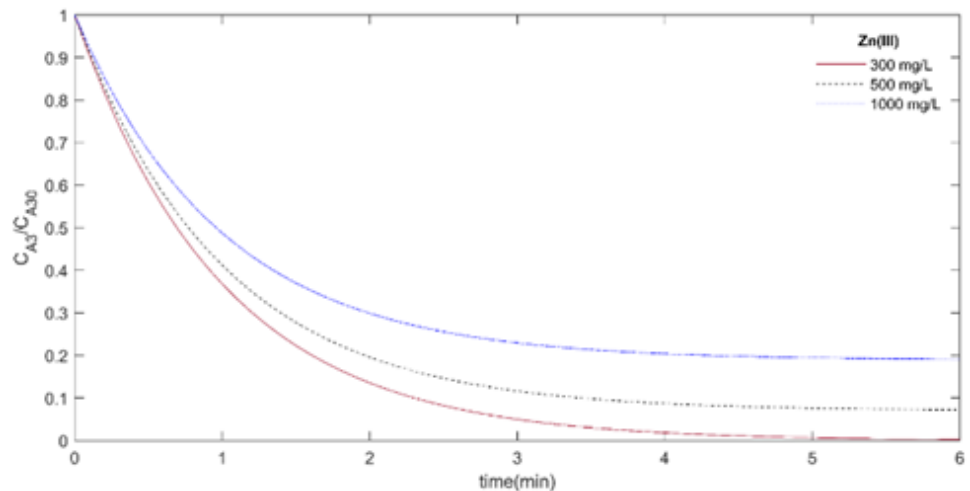

Figure 6 Effect of the initial zinc concentration in the external phase on zinc extraction by model prediction.
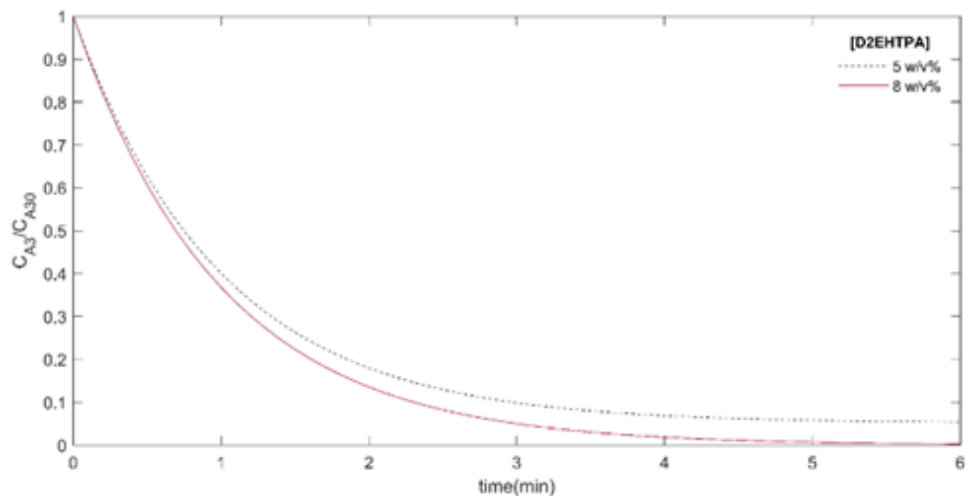

Figure 7 Effect of carrier concentration on zinc extraction by model prediction.

Effect of Stripping Agent Concentration

The effect of stripping agent concentration in zinc extraction was investigated in the range of 1.5–2.5 M H_2SO_4, and the simulated data are presented in Figure 8. The extraction efficiency values at H_2SO_4 concentrations of 1.5, 2.0, and 2.5 M were 92.73%, 94.79%, and 99.75% respectively. This suggests that the increment of stripping agent concentration improves the rate and extraction performance.

The driving force in the ELM process is governed by the hydrogen ion concentration gradient between the external and internal aqueous phases. At a certain level, the increment of stripping agent

concentration will increase the extraction performance due to the chemical potential differences. Moreover, the capacity of the internal phase increases with the increment of stripping agent concentration, thus enhancing the extraction efficiency. A similar result for the effect of stripping agent concentration on the extraction efficiency was reported by Sengupta et al. [27]. However, various reports stated that a further increase in the concentration increases the ionic strength difference between the internal and external phases, resulting in increased membrane swelling and decreased extraction efficiency [8, 23].
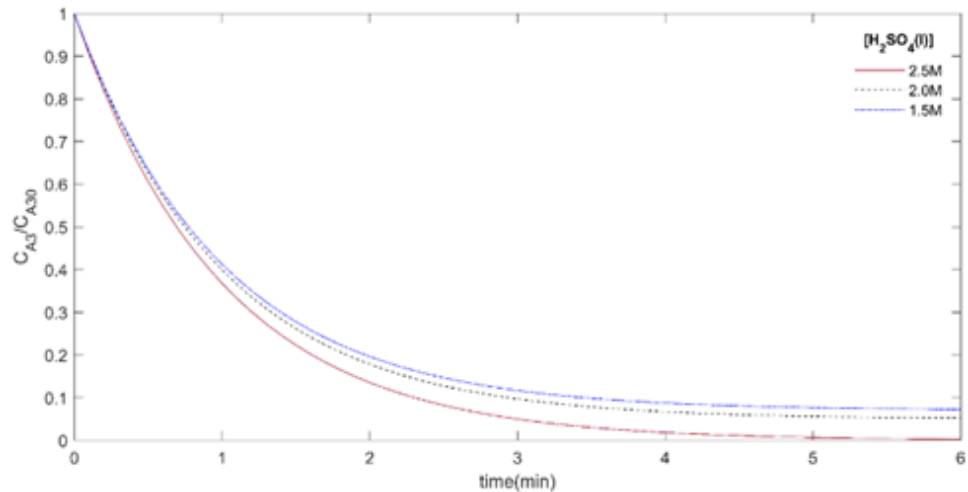

Figure 8 Effect of the initial concentration of sulphuric acid in the internal phase on zinc extraction by model prediction.

Conclusions

MATLAB software was successfully applied to solve the equation model. At the fixed optimum conditions, the predicted extraction efficiency from the simulation shows a small deviation from the experimental data. The effect of several parameters was studied in the model, including the treat ratio, Zn^{2+} concentration at the external phase, carrier concentration, and the stripping agent concentration. The standard mean deviation in the experimental results relative to the simulated ones in the present work was 6.15%. The good agreement between the simulated results and the theoretical study of ELM promotes confidence in the model as a viable prediction tool for zinc extraction using facilitated ELM.

Acknowledgements

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