Empirical Correlation of Emulsion Size Prediction for Zinc Extraction Using Flat Blade Impeller System in Emulsion Liquid Membrane Process

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Abstract In this study, determination of droplets in the presence of blended mixture of surfactants (Span 80 and Tween 80) and nanoparticles, iron (III) oxide (Fe$_2$O$_3$) were investigated using a single stage mixer-settler extractor with 4-pitched flat blade impeller on one shaft employment. Additionally, the influence of Fe$_2$O$_3$ and blended surfactant mixture of Span 80 and Tween 80 on the dispersion of emulsion in terms of Sauter diameter ($D_{32}$) measurement was compared with new correlations. Results indicate that the presence of Fe2O3 in the blended mixture of surfactant simultaneously decreased in $D_{32}$ by 79 % and the stability of the emulsion system was enhanced. Overall, empirical correlation for droplet size at different conditions are obtained, and the modified correlation for $D_{32}$ is presented. The correlation found is $D_{32}/D_{1} = 0.02265(3.419\Phi_i^{-1})W_e^{-0.6}$. The calculated average absolute relative deviation (%AARD) is 2.69 %, thus indicating a good accuracy and acceptability between the presented correlation and experimental data.

Keywords: emulsion liquid membrane, correlation, zinc, flat blade impeller

Introduction

Zinc is considered as a harmful metal due to its toxicity and carcinogenic effects as it is present in large quantities in the environment. The maximum amount of zinc in effluent discharged into aquatic bodies is restricted to 2.16 mg/L by the US Environmental Protection Agency (USEPA) [1]. Many methods have been used to remove zinc. One of the potential methods is emulsion liquid membrane. Emulsion liquid membrane (ELM) is invented by Li [2] in 1968 and has grown to be accepted into unit operation for the separation of contaminants such as metals, weak acids/bases and hydrocarbons [3]. However, ELM is limited as it is unstable in long contact time. The most challenging aspect of commercializing this technology is managing the emulsion stability during the process that includes emulsion breakage and swelling [4].

One of the alternative techniques to overcome the emulsion instability is applying the blended surfactant during the emulsification process. This technique has gained a lot of attention as it may reduce the usage of high surfactant concentration and enhance the flexibility of the formed surfactant layer [5]. Recently, several researchers had found emulsion stability using blended surfactant. For instance, Raji et al. [6]
demonstrated that the mixture of Span 85 and Span 80 could enhance the stability and extraction efficiency. Björkegren et al. [7] evaluated the presence of butanol as a co-surfactant mixed with Span 80 which exhibited a significant effect on the emulsion stability. Another study by Rosly et al. [5] stated that the emulsion stability could enhance the relationship between hydrophilic and lipophilic surfactants as well as their intermolecular interaction.

Currently, particle-stabilized emulsion or Pickering emulsion has received huge attention due to emulsion stability, lower toxicity and easy demulsification. According to Levine et al. [8], the emulsion stability and average droplet size strongly depend on the concentration of the particle. Based on Albert et al. [9], the stability of emulsion can increase from 0.05 to 8.0 % with the presence of particles. Pichot et al. [10] used a very small amount of silica particle as low as 0.2 % to provide long-term stability of emulsion as the particle covered up the interface droplet with tightly packed layers of particles making the droplet against coalescence. Furthermore, the effectiveness of solid particle as a stabilizer in ELM system mainly depends on their wettability. The adsorption rate of a particle at the oil-water interface is greatly influenced by its hydrophobicity depending on the oil-water interface contact angle. For example, Zhou et al. [11] used Fe₃O₄ to stabilize the emulsion and found that the emulsion stability significantly affected non-polar weakly polar oils, where the contact angle is close to 90°.

In addition, the distribution of droplet size and the final droplet size are the effects of a dynamic equilibrium between fractured and coalescence at a particular duration of agitation. It was discovered that the size of emulsion droplets and globules are influenced by the type and number of impellers in the system [12]. Many mechanical stirrer vessels were commonly developed for dispersion of an immiscible liquid phase for mass transfer or emulsifications, solid blending as well as forming of food for food industries [13]. Among them, flat blade impellers are a common choice because of its simplicity [14], and it provides wider vortices and better axial circulation resulting in reduced mixing time [15]. Maaß et al. [16] investigated the effects of the dispersed phase fraction on the evolving drop size distribution in different low viscous liquid/liquid systems by using a flat blade impeller system. The result shows drop sizes were decreasing along with agitation time and increasing with the increment of dispersed phase fraction. Besides that, Jahanzad et al. [17] predicted the average diameter of droplets from the dispersion process using a flat blade impeller system. The degree of droplet stability was evaluated by analysing the coalescence and breakage in corresponding monomer-water dispersion processes. Determination of droplet size is crucial as it is important for modelling of extractor, mass transfer and scale up designs of large industrial processes [18–21]. Thus, numerous investigators studied the drop size of ELM and derived various correlations to predict average droplet diameter in agitated vessels.

Most of the correlations are based on Hinze-Kolmogorov’s theory. According to this theory, only smaller diameters of the energetic eddies compared to the drop size could lead to drop breakage at the initial range of turbulence spectrum [22, 23]. Besides that, this theory was used to predict the impeller speed dependence on the mean drop size. Thus, the predicted equation for Sauter mean diameter ($D_{32}$) is proposed by Equation (1).

$$\frac{D_{32}}{D} = C_1 (1 + C_2 \varphi) We^{-0.6}$$

(1)

Where $C_1$ and $C_2$ are constant, and $\varphi$ is the holdup or dispersed phase volume fraction. Weber number is dimensionless. In this case, Weber number, which is influenced by the stirrer apparatus and usually used to scale up geometric similarities, is defined by the following equation:

$$We = \frac{\rho_c D_l^2 N^2}{\sigma}$$

(2)

Where, $N$ is the impeller speed, $D_l$ is the impeller diameter, $\sigma$ is the interfacial tension and $\rho_c$ is the density of the continuous feed phase.

Three previous correlations were proposed by Mlynek and Resnick [24], Jahanzad et al. [17] and Wang and Calabrese [25] for their system. However, the correlation has a limitation range. Mlynek and Resnick
[24] used a mixture of CCl₄ and iso-octane in the dispersed phase, and distilled water in the continuous phase. In this study, the holdup volume fraction between 0.025 and 0.25 can be fitted well using the correlation in Equation (3).

\[
\frac{d_{32}}{D} = 0.058(1 + 5.4 \Phi)We^{-0.6}
\]  

(3)

Meanwhile, Jahanzad et al. [17] developed a new correlation focusing on the process of suspension polymerization. The correlation provided a range for holdup volume fraction between 0.05 and 0.4 and the predicted equation for Sauter mean diameter proposed in the following form:

\[
\frac{d_{32}}{D} = 0.022(1 + 3.55 \Phi)We^{-0.6}
\]  

(4)

Furthermore, the correlation discovered by Wang and Calabrese [25] also considered Weber number as a function of the stirrer speed and emulsification time. The correlation in Equation (5) was developed.

\[
\frac{d_{32}}{D} = 0.066We^{-0.66} \left[ 1 + 13.8Vi^{0.82} \left( \frac{d_{32}}{D} \right)^{0.33} \right]^{0.59}
\]  

(5)

Wang and Calabrese [25] introduced viscosity vessel number, Vi in the correlation. The holdup volume fraction was less than 0.002 and therefore, the holdup was neglected in the correlation. The correlation is valid for viscosity of dispersed phase, \( \mu_d < 0.5 \) Pa.s where it is applied in the viscosity vessel number:

\[
Vi = \frac{\mu d_{32}}{\sigma} \left( \frac{\rho IS}{\rho d} \right)^{1/2}
\]  

(6)

Where, \( \rho_d \) is the density of the dispersed phase and \( \mu_d \) is the viscosity of the dispersed phase. All these stated correlations were established using a flat blade impeller system and used in this study to compare with the experimental data.

In this work, droplet size was measured to analyse the stability of the emulsion for zinc extraction using blended mixture surfactant and addition of Fe₂O₃ nanoparticles. In order to achieve a better understanding in ELM technique, the effect of several important parameters influencing emulsion stability on \( D_{32} \) were investigated. The formulation of droplet size from the experimental data were manipulated to develop a predicted correlation. To the best of our knowledge, no further studies have been conducted to determine a suitable correlation for predicting \( D_{32} \) in the presence of blended mixture surfactant and nanoparticle for zinc extraction using flat blade impeller in emulsion liquid membrane process.

**Materials and methods**

**Materials**

Palm cooking oil (BURUH) produced by Lam Soon Edible Oils Sdn. Bhd. were used as a diluent. Bis-2-ethylhexyl phosphoric acid (D2EHPA, 95 % purity) and bis(2,4,4-trimethylpentyl)thiophosphinic acid (Cyanex 302, 99 % purity) were obtained from Merck and Sigma-Aldrich, respectively. Span 80 (> 60 % oleic acid), Tween 80 (≥ 58 % oleic acid), sulfuric acid (H₂SO₄, 98 % purity) were procured from Merck. Iron (III) oxide nanoparticle (Fe₂O₃ NPs, < 50nm particle size) as the particle component were purchased from Sigma-Aldrich. Thiourea (SC(NH₂)₂), 99% purity) were obtained from Qrec. All these materials were of analytical grade and used without further purification.
**Methods**

**Preparation of water-in-oil (W/O) emulsion**

The liquid membrane was prepared by dissolving the desired concentration of bis-2-ethylhexyl phosphoric acid (D2HEPA) as an extractant and bis-(2,4,4-trimethylpentyl) thiophosphinic acid (Cyanex 302) as a synergist extractant into palm oil that acts as a diluent. Acidic thiourea in H$_2$SO$_4$ was prepared as an internal aqueous phase. The primary emulsion was prepared by emulsifying equal volumes (10ml) of the organic liquid membrane phase (extractant, Span 80 and Tween 80 in palm oil) and stripping liquid phase (acidic thiourea in H$_2$SO$_4$) using a homogenizer (Heidolph Silent Crusher M).

The primary emulsion stability was determined by manipulating the HLB value of blended surfactant mixture of Span 80 and Tween 80 and the presence of Iron (III) Oxide (Fe$_3$O$_4$) nanoparticle as a stabilizer. Then, parameters incorporated with the emulsion stability will be studied, such as hydrophilic-lipophilic balance (HLB) range (4.3–8.0), blended surfactant mixture concentration (1–7 % w/v), homogenizer speed (5000–12000 rpm), and nanoparticle concentration (0–0.1 % w/v). On the other hand, emulsifying time of 3 minutes will be fixed. The breakage scenario of the emulsion will be determined using Equation (7).

\[
Aqueous\ Phase\ Separation\ (\%) = \frac{Aqueous\ Solution\ (ml)}{Emulsion\ (ml)} \times 100
\]  
(7)

**Measurements and correlation**

The emulsion was freshly prepared for each step of the study to ensure no emulsion coalescence occur. Small drops of W/O emulsion were placed later on the microscope slide to capture the image of the droplets under a polarizing microscope (Olympus CX31, Japan). The microscope was equipped with a camera which captures the emulsion image, and this microscope is linked directly to Video Structure Image Analyzer software (Vimage) on the computer. Direct observation of emulsion is needed to measure the Sauter mean diameter of emulsion. The Sauter mean diameter was calculated using the following equation:

\[
d_{32} = \frac{\sum D_p^3}{\sum D_p^2}
\]  
(8)

Where, $D_p$ is the diameter of each droplet.

In order to predict the size of the emulsion droplet using the correlation in Equation (1), several constant values including interfacial tension, density, viscosity, holdup phase volume fraction, and impeller speed were measured. The viscosity was determined using TLS spindle equipped in a rotational viscometer (Cole-Parmer 98965-40, United States) at room temperature (26 °C).

The interfacial tension of two layers were measured using surface tension meter (KRUSS, easy dyne). The purpose of measuring the interfacial tension is to know the strength of the aqueous phase when dispersed in the organic phase.

Hence, the fitted experimental data in the correlation was selected based on absolute relative deviation (%AARD):

\[
AARE\ (\%) = \frac{1}{NE} \sum_{i=1}^{NE} \left( \frac{(d_{32})_{i}\ exp -(d_{32})_{i}\ calc}{(d_{32})_{i}\ exp} \right) \times 100\%
\]  
(9)

Where $(D_{32})_{i}\ exp$ is the measured Sauter mean diameter from the experiment, NE is the number of experimental data points and $(D_{32})_{i}\ calc$ is the calculated value for Sauter mean diameter from the proposed correlation.
Results and discussion

Prediction of mean droplet size

To introduce a new correlation for the prediction of droplet size in the presence of zinc in the feed phase, the general equation developed by Hinze theory was used to correlate the Sauter mean diameter ($D_{32}$) in this system. In order to determine the constant value, the experimental finding of overall $D_{32}$ was applied in Equation (1) and the following correlation in Equation (10) was achieved with the constant value obtained as follows: $C_1 = 0.02265$ and $C_2 = 3.419$. Figure 1 shows the predicted $D_{32}$ acquired from Equation (10) and the experimental data for dispersion of aqueous in diluent at a difference value of $\phi_i$.

For the reliability analysis of correlation, average absolute relative deviation (%AARD) was calculated from Equation (9). The amount of calculated AARD percentage for this correlation is about 2.69 %, indicating good accuracy and acceptability between the presented correlation and experimental data. However, this correlation has a limitation where the holdup volume range is about 0.43 to 0.50.

$$\frac{D_{32}}{D_1} = 0.02265(3.419\phi_i - 1)We^{-0.6}$$

(10)

Where, $\phi_i$ in the range of 0.43 to 0.5 has been used experimentally.

According to Figure 1, dispersion of aqueous in diluent was carried out with different dispersed phase holdup volume $\phi_i$. Result shows that a smaller droplet size of 2.43 $\mu$m was observed at lower $\phi_i$ (0.43). For lower $\phi_i$ value, the droplet is more stable as the stabilizer covered up the droplet interface and there is less persistent collision. However, upon increasing the $\phi_i$ up to 0.5, the size of the droplet increased to 3.69 $\mu$m as shown in Figure 2. This phenomenon is predominantly due to the frequent collision of droplets which promotes coalescence and increases the droplet size. Hence, it can be deduced that increasing the holdup volume, $\phi_i$ results in larger droplet formation [17, 25].

![Figure 1. Comparison between experimental droplet diameter $D_{32}$ and calculated $D_{32}$ from correlation](image-url)
Effect of Surfactant concentration

Based on variation values of blended surfactant concentration, a comparison between the Sauter mean diameter ($D_{32}$) for experimental and correlation data is illustrated in Figure 3. Surfactants play a crucial role in liquid-liquid dispersion and are used as a stabilizer to protect droplets from coalescence. Throughout this study, increasing the blended surfactant mixture from 4 to 7 % w/v decreases the Sauter mean diameter. Experimental data and the correlation show the droplet size decreases up to 26.4 % and 14.0 %, respectively. According to Hall et al. [25], the Weber number tend to increase with surfactant concentration. Weber number is an important dimensionless value as it is being used to predict the drop size. In this research, the increment of surfactant concentration tend to increase the organic membrane density and decrease the interfacial tension value. Hence, the Weber number will be increase resulting the droplet size decreased. The result is consistent in the experiment data where the increase of the surfactant concentration decrease the droplet size. This can be attributed to more surfactant molecules adsorbed at the interface between the oil membrane and internal phases at higher surfactant concentration. The accumulation of surfactant monolayers reduces the interfacial tension, hence forming smaller droplets. However, it was observed that there was a significant error between the correlation and experimental data of droplet size at surfactant concentration of 4 % w/v. This is due to the dominance of the mixing effect entropy at low surfactant concentration and the surfactant molecules remaining in the solution as monomers [26]. Thus, the emulsion is lacking stability and dispersion with low concentrations led to intensive droplet growth in-situ resulting in large-size droplets.

Figure 3. Effect of surfactant concentration on Sauter Diameter of primary emulsion (Experimental conditions: liquid membrane = palm oil; $[SC(NH_2)_2]$ = 1.0 M; $[H_2SO_4]$ = 0.1 M; HLB = 8, emulsification time = 3 min, organic: internal phase = 1:1, T = 26 ± 1 °C)
**Effect of Homogenizer speed**

Figure 4 states the comparison between the sizes of droplets obtained from the experimental data and developed correlation at different homogenizer speeds of 6000, 8000, 10000 and 12000 rpm. As seen in Figure 4, both graphs show a similar decrement trend with the homogenizer speed; and the absolute average relative deviation percentage (%AARD) is 18.67 %. An increase of homogenizer speed increases the Weber number, thus forming smaller droplet sizes and giving larger numbers of dispersed phase in the system. According to Mulia et al. [27], higher homogenization speeds, higher energy density is exerted on the solution that directly reduces the emulsion droplet size. However, it can be observed that the size of droplet from experimental data did not strictly decrease from homogenizer speed at 8000 to 12000 rpm. This implies that at high homogenizer speed, turbulence occurs as the flow rate of fluid exceeds a critical limit. Resulting in the formation of small eddies generated from turbulence. Small eddies is ineffective because maximum energy is dissipated through viscous losses rather than through droplet disruption. Next, it can be seen that, low homogenizer speed at 6000 rpm crucially diverged from the correlation. Low energy creates low destructive force; thus, inhibiting the activity of stirrer to disperse the water droplets resulting in large droplet formation.

![Figure 4. Effect of homogenizer speed on Sauter Diameter of primary emulsion (Experimental conditions: liquid membrane = palm oil; [SC(NH₂)₂] = 1.0 M; [H₂SO₄] = 0.1 M; HLB = 8, [blended surfactant] = 5 % (w/v), emulsification time = 3 min, organic: internal phase = 1:1, T = 26 ± 1 ℃)](image)

**Effect of Nanoparticle concentration**

Figure 5 shows the effect of nanoparticle concentration towards D₃₂ in this system. It was observed that the trend for the correlation shows no changes as the nanoparticle concentration increases from 0.02 to 0.1 % w/v. The percentage of absolute average relative deviation (%AARD) is 8.4 %. Addition of nanoparticles enhance the density of the organic membrane diluent, hence resulting in the increment of the Weber number. However, the Weber number does not strictly increase as there is a small difference in organic membrane density, which is due to the small number of nanoparticles between 0.02 to 0.1 % w/v. Thus, there were no significant changes in terms of droplet size D₃₂ throughout this study. Meanwhile, the correlation and the experimental data fitted well between 0.0 and 0.06 % w/v. But there was a crucial error at 0.1 % w/v with the percentage of error up to 27.5 %. At 0.1 % w/v and high concentrations of nanoparticles, the droplet achieved maximum coverage of the particles surrounding the droplet interface and the excess is not adsorbed [12]. This implies that nanoparticles take action by adsorbing the oil-water interface and forming densely packed layers on droplets. Thus, resulting in low interfacial tension that led to small droplet formation as the presence of nanoparticles and surfactants simultaneously have the most influence on the interfacial tension.
Figure 5. Effect of nanoparticle concentration on Sauter Diameter of primary emulsion (Experimental conditions: liquid membrane = palm oil; \([\text{SC(NH}_2\text{)}_2]\) = 1.0 M; \([\text{H}_2\text{SO}_4]\) = 0.1 M; HLB = 8, [blended surfactant] = 5 % (w/v); homogenizer speed = 8000 rpm emulsification time = 3 min, organic: internal phase = 1:1, \(T = 26 \pm 1 ^\circ\text{C}\)).

Effect of HLB value

Figure 6 demonstrates the comparison between Sauter mean diameter for experimental data and the correlation based on the difference of the HLB values. The trend for the correlation graph was decreasing from HLB 4.3 to 8. Span 80 and Tween 80 have the same density value of 1.06 g/cm³. However, in this case, the addition of co-surfactant could decrease the interfacial tension by minimizing the repulsion of hydrophilic head-group of surfactants resulting in a significant difference in Weber number. Hence, there are various \(D_{32}\) droplet sizes. The correlation result shows the droplet size at HLB value 4.3 was 3.94 µm. At this point, it has the lowest value of Weber number as the interfacial tension reading was small, hence forming a large droplet size. Meanwhile, increasing the HLB value up to 8 slightly decreased the droplet size due to reduction of the interfacial tension. The (\%AARD) for this study was 21.5 %, which demonstrates a small variation in comparison between the experimental data and the Hinze theory. According to Figure 6, it can be seen that there was a prominent difference of droplet size between the correlation and experimental data at HLB 4.3. Larger droplet size from the experimental data might be due to low adsorption rate of surfactant molecule to interact at the oil-water interface of droplet during the dispersion process. Hence, high surface tension would form and decrease the emulsion viscoelasticity and surface contact area of the droplets resulting in thinner organic membrane layers [5].
Figure 6. Effect of HLB value on Sauter diameter ($D_{32}$) (Experimental conditions: liquid membrane (palm oil); $[\text{SC(NH}_2\text{)2}] = 1.0 \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.1 \text{ M}$; [blended surfactant] = 5 % (w/v); homogenizer speed = 8000 rpm; emulsification time = 3 min; organic: internal ratio phase = 1:1; $T = 26 \pm 1 \text{ °C}$)

Conclusions

A comparative study was carried out on the empirical correlation and experimental data. In this study, the presence of nanoparticle ($\text{Fe}_2\text{O}_3$) and blended surfactant mixture (Span 80 and Tween 80) showed a spectacular effect on the droplet formation. The formation of small droplets was due to several parameters. For instance, providing higher energy intensity in the solution by increasing the homogenizer speed, the surfactant concentration, and the HLB value and decreasing the holdup volume will result in the reduction of interfacial tension and average droplet size up to 79 %. A modified empirical correlation using nanoparticle and blended mixture of surfactant has been derived and fitted well with the experimental data with the limitation range of holdup volume at 0.43 to 0.5. The calculated average absolute relative deviation (%AARD) is about 2.69 %, which indicates good accuracy with the experimental data. From the correlation, it was shown that the Weber number play a vital role in the prediction of droplet diameter. As the Weber number increases, the calculated droplet size decreases. This implies that the Weber number depends on several conditions including interfacial tension, homogenizer speed, diluent density and diameter of impeller.

Acknowledgments

The authors would like to acknowledge the Ministry of Higher Education (MOHE), Universiti Teknologi Malaysia (RU Research Grant; Q.J130000.2451.08G02 and R.J130000.7351.4B427), and Centre of Lipid Engineering and Applied Research (CLEAR) for the financial support that makes this research possible.

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