

Emulsion Liquid Membrane Modelling for Cadmium Removal using Taylor-Couette Column

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ARTICLE INFO	ABSTRACT
Article history: Received 2 September 2023 Received in revised form 17 November 2023 Accepted 28 November 2023 Available online 15 December 2023	Emulsion liquid membrane modelling for cadmium extraction using a counter rotating Taylor-Couette column (TCC) has been done. Lower shear stress in a TCC system is beneficial in preventing emulsion damage while maintaining excellent extraction efficiency. The study used type II facilitated transport of cadmium based on the immobilized hollow spherical globule model. The investigated parameters were HCl
<i>Keywords:</i> Emulsion liquid membrane; Taylor- Couette column; modelling; mass transfer; cadmium extraction	concentration in the external phase (0.05 - 0.5 M), extraction speed (inner cylinder 600 rpm, outer cylinder: 300 - 700 rpm), initial feed concentration (75 - 300 ppm), volume ratio of internal to membrane phase ($1/3 - 1/6$), and volume ratio to of emulsion to feed phase ($1/4 - 1/10$). The model could explain the experimental data very well with an accuracy of more than 95%.

1. Introduction

Very low concentration of contaminants requires effective separation process. Among the available methods, emulsion liquid membrane (ELM) provides selective separation of the contaminants including heavy metals, weak acids/bases, inorganic species and hydrocarbons. The high interfacial area provides higher mass transfer. The requirement of small amount of organic solvent promises high separation efficiency, yet the high ability to remove contaminants. Possibility of reusable organic solvent after demulsification process is significant in managing hazardous materials handling. Previous studies on ELM for removing contaminants have been reported [1-3].

Stable emulsion is a key factor in the successful extraction process. Stable emulsion generated by the incorporation of high surfactant. At specific high surfactant concentrations, smaller emulsion droplets with a high mass transfer area between the external and internal phases can be created by

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reducing the membrane phase's surface tension [4]. However, because the emulsion's viscosity also rises with excessive surfactant concentrations, extraction efficiency is actually decreased [5,6].

Conventional extraction process under stirred vessel commonly employs high extraction speed to enhance extraction efficiency. However, this process disrupts emulsion instability including membrane breakage and emulsion swelling. The broken membrane will release back the entrapped solute to the external phase. Based on the problems related to ELM process, utilisation of Taylor Couette column (TCC) is offered to replace the application stirred tank for extraction process [7,8]. TCC is believed to produce good emulsion stability due to lower shear stress by maintaining high extraction efficiency [9,10]. According to a prior study by Park [11], small gap TCC, in which the outer cylinder is fixed and the inner cylinder rotates, can produce significant extraction efficiencies in a comparatively short contact period. Ahmad *et al.*, [7] also conducted a study that compared the effectiveness of counter-rotated TCC and stirred vessels for the removal of cadmium using ELM. Compared to stirred vessels, counter-rotated TCC reached equilibrium faster and had a greater extraction efficiency [7].

Previous studies on mathematical model for ELM system have been done. Some researchers investigated type II facilitated transport of metal extraction. The model includes reversible reaction at the boundary between feed and stripping phases as well as diffusion through the emulsion globule. Teramoto et al., [12] developed a model by taking into account external phase mass transfer and membrane breakage phenomenon. In the research of Othman et al., [13], the extraction and stripping reaction of chromium and carrier was considered. Liu and Liu [14] expanded the model by investigating the fractional resistances of external phase diffusion as well as emulsion globule diffusion towards the overall process. Type II facilitated transport of arsenic under emulsion liquid membrane was developed by Huang et al., [15] by incorporating mass transfer resistance of external phase and interface of external-membrane phase. Chemical equilibrium of extraction and stripping reactions were also included. The behaviour of extraction process could be predicted and analysed; perturbation method could approximate the solution. Mercury removal supported by dibutylbenzoylthiourea was investigated by Weiss et al., [16]. In the model, mass transfer at the boundary between feed and membrane phases, cadmium-TOA complex diffusion across the membrane phase, and reversible reaction at the boundary between the feed and stripping phases were considered. An unsteady state mathematical models to express type II facilitated transport was elaborated by Banerjea [17] and Chakraborty et al., [18]. Ahmad et al., [19] developed mathematical model for cadmium removal by modifying the models of Huang [15], Lee and Chan [20], and Lee et *al.,* [21].

In general, there are five dimensional models of emulsion globules, namely: i) uniform flat-plate model, ii) hollow sphere model, iii) immobilized hollow sphere model, iv) immobilized spherical globule model, and v) immobilized hollow spherical globule model. The first and second emulsion globule models are reported to be less accurate due to difficulties in determining membrane thickness. Meanwhile, the 5th emulsion globule model is a combination of the 3rd and 4th emulsion globule models in which the emulsion is assumed to be stable [19]. Among the five types of mathematical model related to emulsion globule, immobilized hollow spherical globule model was referred in this study. In this model, the globule contains heterogeneously distributed internal droplets. The droplets surrounded by peripheral membrane layer. Mass transfer take places in three stages of diffusion, i.e. through external boundary layer, peripheral membrane layer, and internal droplet [22]. The model includes mass transfer resistance in the external phase and emulsion globule, stripping reaction, and complex diffusion as described in Figure 1.



Fig. 1. Extraction model of cadmium in ELM process

Based on the literature described above, most studies focus on mathematical modelling of ELM systems using stirred tanks. There is rarely any information regarding mathematical modelling of cadmium extraction using TCC on the ELM system. Therefore, in order to optimise the permeation process using TCC, previous model was applied and developed [19]. This model incorporates some variables influencing the permeation process of cadmium in a counter-rotated Taylor-Couette column. In this study, cadmium was chosen because it is a highly toxic metal [23]. It is known that cadmium can enter the human body through ingestion and inhalation, such as in contaminated food. Cadmium has been linked to kidney damage in the human body. Cadmium, in high doses, can harm the respiratory system. Because of cadmium's toxicity, the recovery procedure is critical.

1.1 Reaction and Chemical Equilibrium

Extractant utilisation is required in cadmium extraction using emulsion liquid membrane. In the process, the extractant acts as facilitator of cadmium diffusion in the emulsion. There is complexation reaction of cadmium and carrier (trioctylamine) in the exterior of emulsion globule. Then, the formed complex diffuses through the organic membrane phase. Figure 2 shows the structure of cadmium-TOA complex. A stripping reaction occurs at the membrane-internal phase interface with the internal reagent present in the internal droplets via a reversible reaction. These reactions are described as follows:

Extraction reaction:

$$CdCl_4^{-2} + 2R_3N + 2H^+ \leftrightarrow CdCl_4(R_3NH)_2$$

or

 $A + 2B + 2H \leftrightarrow C$

Eq. (1) is correlated with experimental results given in Figure 2.

(1)



Stripping reaction:

$$CdCl_4(R_3NH)_2 + 20H^- \leftrightarrow CdCl_4^{-2} + 2R_3N + 2H_2O$$
⁽²⁾

or

$$C + 2OH \leftrightarrow A + 2B$$

Where R_3N represents the carrier and $CdCl_4(R_3NH)_2$ denotes the solute-carrier complex.

The reaction in the internal phase is:

$$CdCl_4^{-2} + 2NH_4^+ \leftrightarrow (NH_4)_2CdCl_4 \tag{3}$$

or

$A + 2NH_4 \leftrightarrow X_{Cd}$

The equilibrium constant for reaction (1) is as follows:

$$K_{eq} = \frac{[C_C]}{[C_A][C_B]^2[C_H]^2}$$
(4)

Due to the stoichiometry for extraction reaction, the following expression holds:

$$C_B^0 = C_B + C_C \tag{5}$$

where C_B^0 is the initial carrier concentration in the organic membrane phase. The substitution of Eq. (5) into Eq. (4) becomes:

$$[C_C]_{r=R} = K_{eq}[C_A][C_H]^2 ([C_B^0] - [C_C]_{r=R})^2$$
(6)

which specifies the solute-carrier complex concentration and optimisation can be performed to find solutions.

For reactions (2) and (3), the equilibrium constant can be expressed respectively as:

$$K_{eq,s} = \frac{[C_A][C_B]^2}{[C_C][C_{OH}]^2}$$
(7)

$$K_{eq,i} = \frac{\left[c_{X_{Cd}}\right]}{\left[c_{A}\right]\left[c_{NH_{4}}\right]^{2}}$$
(8)

Therefore,

 $[C_C] = \frac{[C_A][C_B]^2}{K_{eq,s}[C_{OH}]^2}$ (9)

$$\left[C_{X_{Cd}}\right] = K_{eq,i}\left[C_A\right] \left[C_{NH_4}\right]^2 \tag{10}$$

1.2 Distribution Coefficient

Distribution coefficient (K_D) can be described as the proportion of recovered metal concentration in the membrane phase and residual metal concentration in the feed phase. This is an important parameter in mass transfer equations that describe solute transport between phases. The distribution coefficient has a direct impact on the extraction efficiency in ELM systems. A higher distribution coefficient generally means that the solute is transferred more efficiently from the external phase to the internal phase within the emulsion [24]. Based on Eq. (4), one obtains:

$$K_{eq} = \frac{K_D}{[C_B]^2 [C_H]^2}$$
(11)

or

$$K_D = K_{eq} [R_3 N]^2 [H^+]^2$$
(12)

By taking logarithms on both sides of Eq. (12), the following is obtained:

$$\log(K_D) = \log(K_{eq}) + 2\log([R_3N]) + 2\log([H^+])$$
(13)

or

$$\log(K_D) = \log(K_{eq}) + 2[\log(R_3N) - pH]$$
(14)

The plots of log (K_D) versus log [$R_3N - pH$] will give the intercept of log (K_{eq}).

1.3 Mass Transfer Model

From Figure 1, it can be seen that ELM consists of internal (I), membrane (II), and external (III) phases. Further, R_i , R, and R_μ with respect to the extraction model of cadmium in the ELM process

are the inner radius of the emulsion globule, radius of the emulsion globule, and radius of the internal droplet, respectively.

The model, as shown in Figure 1, has been based on certain assumptions as follows:

- (i) The extraction solution is homogeny that the system has an even Cd²⁺ concentration.
- (ii) The emulsion globule is monodispersed and spherical, the Sauter mean diameter is used to define the diameter of emulsion globule and internal droplets.
- (iii) The internal droplets are motionless and spread out diversely.
- (iv) Membrane breakage and emulsion swelling are inconsiderable.
- (v) The cadmium transport in the organic phase occurs by diffusion, the effective diffusivity in the organic phase is constant.
- (vi) No volume difference in each phase.
- (vii) The very small internal droplets lead to the insignificant mass transfer resistance of organic and stripping phase.

Based on the above assumptions, mass balance in each phase is given below:

(i) Mass balance of cadmium in external phase, modified from equation given by Lee and Chan [20]

rate of diffusion into globules = rate of accumulation

$$\left(V_{I}+V_{II}\right)\left(\frac{3}{R_{i}}\right)D_{e,C}\left.\frac{\partial C_{C,II}}{\partial r}\right|_{r=Ri}=V_{III}\frac{dC_{A,III}}{dt}$$
(15)

where $D_{e,C}$ is effective diffusivity of cadmium-carrier complex in emulsion phase (cm²/s); C_{A,III} is the concentration of cadmium in external phase (mg/L); C_{C,II} is the concentration of cadmium complex in membrane phase (mg/L); V_I, V_{II}, and V_{III} are the volume of internal, membrane, and external phases, respectively (cm³); R_i is the inside radius of globules (cm); (3/R_i) is the ratio of surface area per volume of globule with radius R_i (cm²/cm³).

(ii) Mass balance of cadmium complex in element volume of globules, taken from Lee and Chan [20]

Rate of diffusion in – rate of diffusion out – rate of reaction in internal phase = rate of accumulation in membrane phase

$$4\pi r^2 D_{\rm e,C} \left. \frac{\partial C_{C,II}}{\partial r} \right|_{r=r+\Delta r} - 4\pi r^2 D_{\rm e,C} \left. \frac{\partial C_{C,II}}{\partial r} \right|_{r=r} - 4\pi r^2 \Delta r \phi_I R_x = 4\pi r^2 \Delta r \phi_{II} \left. \frac{\partial C_{C,II}}{\partial t} \right|_{t=r}$$
(16)

where Δr is the thickness of the element volume (cm); Rx is the stripping reaction rate (mg/cm³/s); ϕ_I and ϕ_{II} are volume fraction of internal phase and membrane phase in the globules, respectively. ϕ_I and ϕ_{II} are calculated as follows:

$$\phi_I = \frac{V_I}{V_I + V_{II}} \tag{17}$$

$$\phi_{II} = \frac{V_{II}}{V_I + V_{II}} = 1 - \phi_I \tag{18}$$

Dividing Eq. (16) with $4\pi r^2 \Delta r$ and limiting Δr to zero, give

$$\lim_{\Delta r \to 0} \left(\frac{D_{e,C}}{r^2} \frac{\left(r^2 \frac{\partial C_{C,II}}{\partial r} \Big|_{r=r+\Delta r} - r^2 \frac{\partial C_{C,II}}{\partial r} \Big|_{r=r} \right)}{\Delta r} - \phi_I R_x = \phi_{II} \frac{\partial C_{C,II}}{\partial t} \right)$$
(19)

Thus,

$$\frac{D_{e,C}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{C,II}}{\partial r}\right) - \phi_I R_x = (1 - \phi_I)\frac{\partial C_{C,II}}{\partial t}$$
(20)

Expanding the differential

$$\frac{D_{e,C}}{r^2} \left(r^2 \frac{\partial^2 C_{C,II}}{\partial r^2} - 2r \frac{\partial C_{C,II}}{\partial r} \right) - \phi_I R_x = (1 - \phi_I) \frac{\partial C_{C,II}}{\partial t}$$
(21)

(iii) Mass balance of cadmium in internal phase [15]

$$V_I R_x = V_I \frac{\partial C_{A,I}}{\partial t}$$
(22)

where $C_{A,I}$ is the concentration of cadmium in internal phase (mg/L).

(iv) Chemical equilibrium

Instead of Eq. (11) and Eq. (12), the chemical equilibrium between cadmium and cadmium complex concentration at the surface of the globules can also be determined in the following equation, as modified from the equation of Huang *et al.*, [15] and Fan *et al.*, [25]:

$$C_{C,II}^* = K_D C_{A,III}^*$$
(23)

With K_D is the extraction distribution coefficient; $C^*_{A,III}$ and $C^*_{C,II}$ are the concentration of cadmium and cadmium complex at the globules surface respectively (mg/L).

Similarly, at the surface of internal phase, the following relationship represents the equilibrium between the concentration of cadmium and cadmium complex according to equation given by Huang *et al.*, [15] and Fan *et al.*, [25]:

$$C_{A,I} = K_{D,I}C_{C,II} \tag{24}$$

where $K_{D,I}$ is the stripping distribution coefficient; $C_{A,I}$ and $C_{C,II}$ are the concentration of cadmium and cadmium complex in the surface of internal phase, respectively (mg/L).

(v) Simplifying the model

By applying the chemical equilibrium between internal phase and membrane phase (Eq. (24)), Eq. (21) and Eq. (22) can be combined thus simplify the model.

$$\frac{D_{e,C}}{r^2} \left(r^2 \frac{\partial^2 C_{C,II}}{\partial r^2} - 2r \frac{\partial C_{C,II}}{\partial r} \right) - \phi_I K_{D,I} \frac{\partial C_{C,II}}{\partial t} = (1 - \phi_I) \frac{\partial C_{C,II}}{\partial t}$$
(25)

Rearranging Eq. (25), give:

$$D_{e,C} \frac{\partial^2 C_{C,II}}{\partial r^2} - \frac{2D_{e,C}}{r} \frac{\partial C_{C,II}}{\partial r} = \left(1 - \phi_I + \phi_I K_{D,I}\right) \frac{\partial C_{C,II}}{\partial t}$$
(26)

(vi) Initial conditions and boundary conditions

Initial conditions are as follows:

$$At t = 0$$

$$C_{A,III} = C_{A,III}^{0}$$
(27)

For all r

$$C_{C,II} = C_{C,II}^0 \tag{28}$$

Boundary conditions based on Lee and Chan [20] are as follows:

For $r = R_i$, at all t

$$D_{e,C} \frac{\partial C_{C,II}}{\partial r}\Big|_{r=Ri} = k_m \left(C_{C,II}^* - C_{C,II} \Big|_{r-Ri} \right)$$

$$= k \left(C_{A,III}^i - C_{A,III}^* \right)$$

$$= k_L \left(C_{A,III} - C_{A,III}^i \right)$$

$$= K \left(C_{A,III} - \frac{1}{K_D} C_{C,II} \Big|_{r-Ri} \right)$$
(29)

where k_m , k, k_L are the mass transfer coefficients in the thin oil membrane layer, interfacial, and external phase, respectively; K is overall mass transfer coefficient; $C_{A,III}^{i}$ is the concentration of cadmium in the interfacial layer.

For r = 0, at all t

$$\left. \frac{\partial C_{C,II}}{\partial r} \right|_{r=0} = 0 \tag{30}$$

(vii) Dimensionless form

In order to avoid mistakes due to conflicting unit, the model equations are transformed into dimensionless form.

Combining Eq. (15) with Eq. (29) resulted in the following dimensionless form [15,25]:

$$K_0(U_{III} - U_{II}|_{x=1}) = \frac{dU_{III}}{d\zeta}$$
(31)

(27)

The dimensionless form of Eq. (26) is:

$$\frac{\partial^2 U_{II}}{\partial x^2} - \frac{2}{x} \frac{\partial U_{II}}{\partial x} = \Omega \frac{\partial U_{II}}{\partial \zeta}$$
(32)

Initial conditions, at $\zeta = 0$

$$U_{III} = 1 \tag{33}$$

$$U_{II} = \frac{C_{C,II}^0}{K_D C_{A,III}^0}$$
(34)

Boundary conditions,

At x = 1

$$G \left. \frac{dU_{II}}{dx} \right|_{x=1} = (U_{III} - U_{II}|_{x=1})$$
(35)

and at x = 0

$$\left. \frac{dU_{II}}{dx} \right|_{x=0} = 0 \tag{36}$$

The definition of each dimensionless variables is described below.

$$U_{III} = \frac{C_{A,III}}{C_{A,III}^0} \tag{37}$$

$$U_{II} = \frac{C_{C,II}}{K_D C_{A,III}^0} \tag{38}$$

$$\zeta = \frac{D_{\rm e,C} t}{R_i^2} \tag{39}$$

$$x = \frac{r}{R_i} \tag{40}$$

$$K_0 = \frac{R_i K}{D_{e,C}} 3 \frac{V_I + V_{II}}{V_{III}}$$
(41)

$$\Omega = 1 - \phi_I - \phi_I K_{D,I} \tag{42}$$

$$G = \frac{K_D D_{e,C}}{R_i K}$$
(43)

1.4 Numerical Solution

The numerical method of lines approach was employed to find the solution of the above partial differential equations and to transform each partial differential equation into ordinary differential equations based on the discretisation of the spatial derivative. Figure 3 depicts that emulsion globule radius is separated into n intervals or (n+1) points.



Fig. 3. Separation of emulsion globule radius into *n* interval for numerical analysis [19]

Numerical derivation of Eq. (31) and Eq. (32) using finite difference method yields the following.

$$\frac{\partial U_{II}}{\partial x} = \frac{U_{II,j+1} - U_{II,j}}{\Delta x}$$
(44)

$$\frac{\partial^2 U_{II}}{\partial x^2} = \frac{U_{II,j-1} - 2U_{II,j} + U_{II,j+1}}{\Delta x^2}$$
(45)

with

$$\Delta x = \frac{1}{n} \tag{46}$$

 $x_j = (j-1)\Delta x$ (47) Therefore, Eq. (31) becomes,

$$K_0(U_{III} - U_{II,n+1}) = \frac{dU_{III}}{d\zeta}$$
(48)

and Eq. (32) becomes,

$$\frac{U_{II,j+1} - 2U_{II,j} + U_{II,j-1}}{\Delta x^2} + \frac{2}{x_j} \frac{(U_{II,j+1} - U_{II,j})}{\Delta x} = \Omega \frac{dU_{II,j}}{d\zeta}$$
(49)

for j = 2 to n, with initial conditions

$$U_{II,j} = \frac{C_{II}^{0}}{\kappa_{D} C_{III}^{0}}$$
(50)

and boundary conditions

$$G \frac{U_{II,n+1} - U_{II,n}}{\Delta x} = (U_{III} - U_{II,n+1})$$
(51)

$$\frac{U_{II,2} - U_{II,1}}{\Delta x} = 0$$
(52)

These arithmetic equations are then utilised to calculate $U_{II,n+1}$ and $U_{II,1}$.

These *n* variables ordinary differential equations (Eq. (48) and Eq. (49)), using their respective initial conditions were solved simultaneously by Runge-Kutta fourth degree using MATLAB software.

1.5 Model Parameters 1.5.1 Effective diffusivity

Wilke-Chang equation was used to determine cadmium diffusivity in the internal (D_l) and membrane phase (D_{ll}) [26].

$$D = 7.4x 10^{-8} \frac{TM^{1/2}}{\eta V^{0.6}}$$
(53)

where T is the temperature (K), M is the molecular weight of solvent, η is the viscosity of solution (cP), and V is the molal volume of solute.

Eq. (53) was used to determine D_l and $D_{ll'}$ It was calculated that D_l was 1.427 x 10⁻⁰⁵ cm²/s and $D_{ll'}$ was 4.315 x 10⁻⁰⁶ cm²/s. Jefferson-Witzell-Sibbelt equation was applied to define the effective diffusivity of complex in the organic phase ($D_{e,C}$) [20].

$$D_{e,C} = D_{II} \left\{ 1 - \frac{\pi}{4(1+2p)^2} \right\} + \frac{\pi}{4(1+2p)} \left(\frac{D_{II}D_A}{D_{II}+2pD_A} \right)$$
(54)

where

$$D_{A} = \frac{2(D_{I}/K_{D,I})D_{II}}{D_{I}/K_{D,I} - D_{II}} \left\{ \frac{D_{I}/K_{D,I}}{D_{I}/K_{D,I} - D_{II}} ln\left(\frac{D_{I}}{K_{D,I}D_{II}}\right) - 1 \right\}$$
(55)

and

$$p = 0.403\phi_I^{-1/3} - 0.5 \tag{56}$$

1.5.2 Mass transfer coefficient

Based on the operating condition, Skelland and Lee equation was utilised to calculate external mass transfer coefficient k_{L} [20].

$$k_L = (ND_{III})^{1/2} \times 2.932 \times 10^{-7} \phi_e^{-0.508} \left(\frac{d_i}{Z}\right)^{0.548} Re^{1.371}$$
(57)

In which, *N* denotes the extraction speed (rps), d_i denotes the impeller diameter (cm), ϕ_e denotes the volume ratio of emulsion to feed phase, D_{III} denotes the diffusivity of cadmium in the external phase (cm²/s), *Z* denotes the tank diameter (cm), and *Re* denotes Reynolds number.

The mass transfer coefficient of the oil phase membrane (k_m) was calculated using equation of Lee and Chan [20] which depends on the used emulsion composition.

$$k_m = \frac{D_{II}}{(R/R_i)(R-R_i)} \tag{58}$$

The interfacial mass transfer coefficient (*k*) was estimated using Loosemore and Prosser equation to be 0.04230 cm/s [27].

$$k = v \times 61Sc^{-0.92}$$
(59)

where v is the kinematic viscosity of surfactant (cm²/s) and Sc is Schmidt number.

Finally, the overall mass transfer resistance is calculated as follow:

$$\frac{1}{K} = \frac{1}{k_L} + \frac{1}{k} + \frac{1}{K_D \cdot k_m} \tag{60}$$

1.5.3 Emulsion diameter

Sauter diameter (d_{32}), reflects the average surface diameter, could be used to express droplet and globule diameter. Emulsion size was governed by emulsion composition as well as processing parameters.

Rotation speed and emulsion characteristics govern the size distribution of emulsion globules. Reis and Carvalho [28] determined emulsion globules size as a function of rotation speed as bellows:

$$\log(d_{32}) = -(1.4 \pm 0.2)\log(N) - 2.4 \tag{61}$$

In which the Sauter mean diameter of emulsion globules, d_{32} , is given in meter and the extraction speed, N, is given in rps.

1.5.4 Extraction distribution coefficient

In the model calculation, extraction distribution coefficient K_D is assumed to be a constant and this fact is true when excess extractant R_3N and buffer are used. When the extractant concentration is much larger than the metal-extractant complex, $[R_3N] >> [CdCl_4(R_3NH)_2]$, the change of extractant concentration $[R_3N]$ during the reaction is not very large and the concentration of extractant is assumed constant. This approach has also been adopted in previous studies [7,29,30]. Using Eq. (14), the extraction distribution coefficient can be calculated.

2. Research Procedure

2.1 Reagents

This experiment applied water-in-oil-in-water (W/O/W) emulsion. The emulsion produced using Span 80 (Merck) as stabiliser. As mobile carrier, trioctylamine (TOA) from Merck was used. Low odour kerosene from Sigma Aldrich was used as diluent. For internal phase, ammonia solution from Merck was used. Feed solution was prepared using cadmium chloride from Sigma Aldrich. To ionise the complex of cadmium-TOA and to set the pH of feed solution, hydrogen chloride (HCI) from Merck was used. Analytical grade chemicals were used in this research without further purification.

2.2 Emulsification Process

The emulsification process was done in double glass beakers; the inner glass contains the emulsion solution, while the outer glass contains ice for cooling of the emulsification cell. A 22.5 kHz ultrasonic irradiation (ultrasonic USG-150) equipped with a titanium horn (3 mm diameter) was used to blend the membrane and internal phase solution. The membrane phase solution (TOA, kerosene, and Span 80) was mixed using magnetic stirrer at 500 rpm for 5 min. The internal phase solution was then added to the prepared membrane phase. The mixture was then emulsified using the ultrasonic probe as shown in Figure 4(a). Experimental condition of emulsification is shown in Table 1.

2.3 Extraction Process

Cadmium chloride was dissolved in deionized water to prepare feed solution. Certain amount of HCl was added to the prepared feed solution to set the pH. Cadmium and HCl concentrations were varied to investigate their effect to extraction process. The prepared emulsion was then added into the feed solution and stirred for cadmium extraction. Applying TCC for cadmium extraction as shown in Figure 4(b), the inner cylinder was maintained at 600 RPM while the outer cylinder speed was varied from 300 rpm to 700 rpm. This extraction speed range can be chosen to ensure adequate mixing and mass transfer between the phases involved in the extraction. Previous researches show that this extraction speed range provides low shear stress, thus preventing emulsion damage [7,10]. During extraction process, sample was taken for every predetermined time. The mixed extraction solution was let for settling for 5 minutes after extraction. Sample was taken from the lower layer to analyse the cadmium concentration and membrane breakage.



Fig. 4. Schematic diagram and photographic of: (a) ultrasound emulsification, and (b) TCC extraction

Table 1

Experimental conditions	
Parameters	Values
Emulsification:	
Span 80 concentration	4 wt. %
TOA concentration	4 wt. %
Ammonia solution in internal phase	0.1 M
Emulsification time	15 min
Extraction:	
Cd concentration in feed solution	75 – 300 ppm
HCl concentration in external phase	0.05 – 0.5 M
Extraction speed of TCC	Outer cylinder: 300-700 rpm
	Inner cylinder: 600 rpm
Volume Ratio of Internal to Membrane Phase	1/3 - 1/6
Volume Ratio of Emulsion to Feed Phase	1/4 - 1/10
Extraction time	0.5 – 35 min

2.4 Analytical Procedures

Diameter of W/O emulsion was determined using Olympus optical microscope equipped with camera. The results were then analysed using image analyser. The Sauter mean diameter of emulsion droplets was found to be 0.877 μ m. The microphotograph of emulsion droplets is given in Figure 5.



Fig. 5. Microphotograph of emulsion droplets

In the range of extraction speed from 300 rpm to 700 rpm, the Sauter mean diameter of emulsion globules was determined based on Eq. (61), which are in the range of 0.42 - 0.13 mm.

Cadmium content analysis was implemented to specify the success of extraction process. AAS model Shimadzu AA-6650 was utilised in this study. Fisher Scientific Accumet AB15+ was used to measure the solution pH.

3. Results and Discussion

The following is a comparison of experimental and estimated data. Various treatments were applied to the study. Solid line and dot lines display the estimated and experimental data, respectively.

3.1 Effect of HCl Concentration in External Phase

Investigation on the influence of acid concentration in the external phase towards the extraction process was carried out using HCl at various concentrations of 0.05 M, 0.1 M, and 0.5 M. Figure 2 revealed the increment of extraction degree by the increase of acid concentration. In the condition when concentration of solute in the feed and stripping phases are about the same, the driving force of diffusion process is pH gradient of both phases. Concentration gradient maintains the high extraction rate. In this circumstance, pH gradient acts to assure the persistence diffusion process. Cadmium ionization was also determined by HCl concentration in external phase. This is due to the fact that basic carrier such as TOA could only pairs well to ionized metal, like CdCl4²⁻. Precise H⁺ concentration is important to confirm the cadmium ion formation. Figure 6 shows that regarding to the metal – carrier formation of cadmium and TOA, HCl concentration of higher than 0.1 M was needed to obtain optimal extraction rate. This is in accordance with Eq. (12) that expresses the increase of distribution coefficient (K_D) at higher HCl concentration. The K_D values were 1.538, 10.471, and 22.305 at HCl concentration of 0.05 M, 0.1 M, and 0.5 M, respectively. It also implies that more cadmium was transported through organic membrane phase. This finding is supported by previous study of Mohammed and Jaber [31]. It was found that acidity of the feed solution governed the extraction efficiency.



Fig. 6. Profile of extraction rate as the effect of HCl concentrations

3.2 Effect of Extraction Speed

Figure 7 describes the effect of extraction speed to cadmium extraction. Parameter of extraction speeds were investigated at 300, 500, 600, and 700 rpm. It was indicated that the increase of extraction speed could accelerate extraction rate. As illustrated by Eq. (57), the transport of cadmium complex from external phase to the interface of external-membrane phase was accelerated at higher extraction speed. As the functions of extraction speed, Reynolds number and external mass transfer coefficient were also enhanced by the increase of extraction speed. It was revealed that lower extraction rate was achieved at extraction speed of 300 rpm represented the occurrence of slow mass transfer. Increasing extraction speed to be 500 rpm could accelerate the equilibrium at 3 min. The highest efficiency was obtained at 600 rpm with equilibrium in 1 min of extraction. Moreover,

extraction efficiency was also governed by d_{32} in which smaller diameter was resulted by higher extraction speed that in turn led to higher efficiency as described in Eq. (61). As previously stated, tiny emulsion is very recommended due to the larger mass transfer area, resulted in the high amount of extracted solute. Nevertheless, accelerating extraction speed until 700 rpm, induced higher membrane breakage of 4.38% thus the captured solute released back to feed phase. Although extraction speed is an important factor governing recovery process, excessive extraction speed induced emulsion instability thus adversely affected extraction efficiency [32,33].



Fig. 7. Profile of extraction rate as the effect of extraction speed

3.3 Effect of Initial Feed Concentration

In the cadmium extraction, mass transfer process was determined by concentration difference of cadmium in feed and stripping phase that acted as the driving force. Effect of initial feed concentration was investigated at 75, 150, and 300 ppm. Even though these comparatively larger sample concentrations are not currently observed in the natural environment, they are employed not only for instrument sensitivity concerns but also to represent extreme scenarios that aid in understanding the potential of the deployed ELM system. Several earlier research have also employed a similar strategy [34-36]. Figure 8 reveals the comparison of estimation and experimental data as the impact of initial feed phase concentration. It was indicated that increasing cadmium concentration in the external phase from 75 ppm to 150 ppm accelerated the extraction rate. However, the increase of cadmium concentration to be 300 ppm actually lowered the extraction rate. This is in line with the research of Davoodi-Nasab et al., [37] that the increase of Gd(III) led to the reduction of extraction efficiency. Figure 8 shows that fast extraction occurred at initial concentration of 150 and 300 ppm, however, lower degree of concentration was generated by system with 75 ppm of cadmium. This phenomenon approved the presumption the importance of concentration difference in extraction process. In the beginning, higher cadmium concentration yielded in higher driving force. System with higher initial concentration reached faster equilibrium. The finding and model matched up very well.



Fig. 8. Profile of extraction rate as the effect of initial cadmium concentrations

3.4 Effect of Volume Ratio of Internal to Membrane Phase

Model of cadmium extraction under emulsion liquid membrane was also studied by effect of volume ratio of internal to membrane phase at 1/3, 1/4, and 1/6, as given in Figure 9. Varying volume ratio of internal to membrane phase resulted in different emulsion characteristics, including size, stability, and extraction capacity. Proper emulsion diameter could be obtained by optimal phase ratio. Entire stripping phase could not be completely enclosed by small amount of membrane phase that in turn generated bigger emulsion globule. The big emulsion globule tends to have thin membrane thus increase the possible membrane breakage. Conversely, higher volume of membrane phase resulted in thicker emulsion membrane thus inhibit extraction process due to the longer diffusion path [33,38]. This condition will decline the transfer rate of cadmium. Decreasing internal to membrane phase ratio led to the fast and remarkable swelling phenomenon, followed by the coalescence of the internal droplet [39]. It was found that volume ratio of ¼ generated the best result. As given in Eq. (61), smaller emulsion globule is more preferable for providing higher mass contact area at the same volume, meanwhile lower k_m was obtained at bigger emulsion size as implicated from Eq. (58). The k_m values were calculated and found to be 0.161, 0.225, and 0.076 at volume ratio of internal to membrane phase of 1/3, 1/4, and 1/6, respectively. Thereby, the study revealed the k_m value was in the order of 1/3 < 1/6 < 1/4.



Fig. 9. Profile of extraction rate as the effect of volume ratio of internal to membrane phase

3.5 Effect of Volume Ratio of Emulsion to Feed Phase

Figure 10 provides the profile of cadmium extraction due to the effect of volume ratio of emulsion to external phase. The figure inferred that degree of extraction was significantly enhanced by the increase of volume ratio of emulsion to feed phase. As reflected by Eq. (15), higher emulsion volume provides more emulsion globule thus increase the interfacial area between feed and emulsion phase. Rearranging Eq. (15), obtained:

$$\frac{dC_{A,III}}{dt} = -\frac{(V_I + V_{II})}{V_{III}} \left(\frac{3}{R_i}\right) D_{e,C} \left.\frac{\partial C_{C,II}}{\partial r}\right|_{r=Ri}$$
(63)

More emulsion supplied more stripping agent thus increase the stripping capacity [40,41]. However, higher emulsion volume would be uneconomical. In this study, volume ratio of 1/6 generated the fastest extraction rate. At higher treat ratio of ¼, bigger emulsion diameter was produced thus actually lowered the extraction rate [42].



Fig. 10. Profile of extraction rate as the effect of volume ratio of emulsion to feed phase

4. Conclusion

The experimental data show the effectiveness of TCC system for ELM application. The research results revealed that the use of TCC provided more attractive results in terms of extraction efficiency. In this system, extraction efficiency reaches 98% in 3 minutes. The low shear stress in TCC provides advantages in terms of emulsion stability during the extraction process. Moreover, the study was succeeded in applying a model of type II facilitated transport of cadmium based on the immobilized hollow spherical globule model for cadmium extraction under TCC. The model considered the mass transfer resistance in the feed phase and emulsion globule, stripping reaction, and complex diffusion. The model could explain the experimental data very well with an accuracy of more than 95%.

References

- [1] Gupta, Smita, Pritam B. Khandale, and Mousumi Chakraborty. "Application of emulsion liquid membrane for the extraction of diclofenac and relationship with the stability of water-in-Oil emulsions." *Journal of Dispersion Science* and Technology 41, no. 3 (2020): 393-401. <u>https://doi.org/10.1080/01932691.2019.1579655</u>
- [2] Karmakar, Rajib, Pritam Singh, Aparna Datta, and Kamalika Sen. "Emulsion liquid membrane in the selective extraction of Dy." *Chemical Engineering Research and Design* 187 (2022): 497-506. <u>https://doi.org/10.1016/j.cherd.2022.09.001</u>
- [3] Raval, Akash R., Himanshu P. Kohli, and Omprakash K. Mahadwad. "A comprehensive review on green emulsion liquid membrane and its applicability towards the removal of contaminants from the aquatic streams." *Water, Air,* & Soil Pollution 233, no. 9 (2022): 379. <u>https://doi.org/10.1007/s11270-022-05849-6</u>
- [4] Raval, Akash R., Himanshu P. Kohli, and Omprakash K. Mahadwad. "Application of emulsion liquid membrane for removal of malachite green dye from aqueous solution: Extraction and stability studies." *Chemical Engineering Journal Advances* 12 (2022): 100398. <u>https://doi.org/10.1016/j.ceja.2022.100398</u>
- [5] Perumal, Murugan, Bhuvaneshwari Soundarajan, and Nihal Thazhathuveettil Vengara. "Extraction of Cr (VI) by pickering emulsion liquid membrane using amphiphilic silica nanowires (ASNWs) as a surfactant." *Journal of Dispersion Science and Technology* 40, no. 7 (2019): 1046-1055. <u>https://doi.org/10.1080/01932691.2018.1496829</u>
- [6] Shirasangi, Rahulkumar, Himanshu P. Kohli, Smita Gupta, and Mousumi Chakraborty. "Separation of Methylparaben by emulsion liquid membrane: Optimization, characterization, stability and multiple cycles studies." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 597 (2020): 124761. <u>https://doi.org/10.1016/j.colsurfa.2020.124761</u>

- [7] Ahmad, A. L., Adhi Kusumastuti, M. M. H. Shah Buddin, C. J. C. Derek, and B. S. Ooi. "Emulsion liquid membrane based on a new flow pattern in a counter rotating Taylor-Couette column for cadmium extraction." *Separation and Purification Technology* 127 (2014): 46-52. <u>https://doi.org/10.1016/j.seppur.2014.02.029</u>
- [8] Zaulkiflee, N. D., M. M. Shah Buddin, and A. L. Ahmad. "Extraction of acetaminophen from aqueous solution by emulsion liquid membrane using Taylor-Couette column." *International Journal of Engineering* 31, no. 8 (2018): 1413-1420. <u>https://doi.org/10.5829/ije.2018.31.08b.33</u>
- [9] Park, Y., L. J. Forney, J. H. Kim, and A. H. P. Skelland. "Optimum emulsion liquid membranes stabilized by non-Newtonian conversion in Taylor-Couette flow." *Chemical Engineering Science* 59, no. 24 (2004): 5725-5734. <u>https://doi.org/10.1016/j.ces.2004.06.015</u>
- [10] Qudus, Nur, Adhi Kusumastuti, Samsudin Anis, and Abdul Latif Ahmad. "Emulsion liquid membrane for lead removal: intensified low shear extraction." *International Journal of Innovation and Learning* 25, no. 3 (2019): 285-295. <u>https://doi.org/10.1504/IJIL.2019.10019205</u>
- [11] Park, Yonggyun. Development and optimization of novel emulsion liquid membranes stabilized by non-newtonian conversion in taylor-couette flow for extraction of selected organic and metallic contaminants. Georgia Institute of Technology, 2006.
- [12] Teramoto, Masaaki, Tsutomu Sakai, Kouyou Yanagawa, Motoyuki Ohsuga, and Yoshikazu Miyake. "Modeling of the permeation of copper through liquid surfactant membranes." *Separation Science and Technology* 18, no. 8 (1983): 735-764. <u>https://doi.org/10.1080/01496398308068577</u>
- [13] Othman, Norasikin, Norul Fatiha Mohamed Noah, Raja Norimie Raja Sulaiman, Norela Jusoh, and Wan Ting Tan. "Emulsion liquid membrane modeling for chromium removal from electroplating wastewater using TOMAC as a carrier." Water Environment Research 93, no. 9 (2021): 1669-1679. <u>https://doi.org/10.1002/wer.1551</u>
- [14] Liu, Xingrong, and Dongshan Liu. "Mass transfer resistance analysis of L-tryptophan extraction in an emulsion liquid membrane system." Separation Science and Technology 35, no. 16 (2000): 2707-2724. <u>https://doi.org/10.1081/SS-100102364</u>
- [15] Huang, Ching-Rong, Huifang Fan, and Dingwei Zhou. "A closed-form solution for a mathematical model of emulsion liquid membrane." *Journal of Membrane Science* 339, no. 1-2 (2009): 233-238. <u>https://doi.org/10.1016/j.memsci.2009.05.008</u>
- [16] Weiss, Siegfried, Valerie Grigoriev, and Peter Mühl. "The liquid membrane process for the separation of mercury from waste water." *Journal of Membrane Science* 12, no. 1 (1982): 119-129. <u>https://doi.org/10.1016/0376-7388(82)80008-2</u>
- [17] Banerjea, S., S. Datta, and S. K. Sanyal. "Mass transfer analysis of the extraction of Cr(VI) by liquid surfactant membrane." *Separation Science and Technology* 35, no. 4 (2000): 483-501.
- [18] Chakraborty, Mousumi, Chiranjib Bhattacharya, and Siddhartha Datta. "Mathematical modeling of simultaneous copper (II) and nickel (II) extraction from wastewater by emulsion liquid membranes." *Separation Science and Technology* 38, no. 9 (2003): 2081-2106. <u>https://doi.org/10.1081/SS-120020136</u>
- [19] Ahmad, A. L., A. Kusumastuti, M. M. H. S. Buddin, D. C. J. Derek, and B. S. Ooi. "Emulsion liquid membrane for cadmium removal: Experimental results and model prediction." *Jurnal Teknologi* 65, no. 4 (2013): 17-24. <u>https://doi.org/10.11113/jt.v65.2321</u>
- [20] Lee, Chau J., and Chih C. Chan. "Extraction of ammonia from a dilute aqueous solution by emulsion liquid membranes. 2. Theory and mass-transfer model." *Industrial & Engineering Chemistry Research* 29, no. 1 (1990): 101-105. <u>https://doi.org/10.1021/ie00097a015</u>
- [21] Lee, Sang Cheol, Byoung Sung Ahn, and Won Kook Lee. "Mathematical modeling of silver extraction by an emulsion liquid membrane process." *Journal of Membrane Science* 114, no. 2 (1996): 171-185. <u>https://doi.org/10.1016/0376-7388(95)00315-0</u>
- [22] Chan, Chih Chieh, and Chau Jen Lee. "Mechanistic models of mass transfer across a liquid membrane." Journal of Membrane Science 20, no. 1 (1984): 1-24. <u>https://doi.org/10.1016/S0376-7388(00)80720-6</u>
- [23] Wang, Ruoyu, Panting Sang, Yahui Guo, Ping Jin, Yuliang Cheng, Hang Yu, Yunfei Xie, Weirong Yao, and He Qian.
 "Cadmium in food: Source, distribution and removal." *Food Chemistry* 405 (2023): 134666. <u>https://doi.org/10.1016/j.foodchem.2022.134666</u>
- [24] Ahmad, Abdul Latif, Zulfida Mohamad Hafis Mohd Shafie, Nur Dina Zaulkiflee, and Wen Yu Pang. "Preliminary Study of emulsion liquid membrane formulation on acetaminophen removal from the aqueous phase." *Membranes* 9, no. 10 (2019): 133. <u>https://doi.org/10.3390/membranes9100133</u>
- [25] Fan, Huifang, Haiyun Zhang, Hui Xie, and Shilin Qu. "Singularity in a mathematical model of emulsion liquid membrane." Applied Mathematical Modelling 36, no. 8 (2012): 3736-3742. <u>https://doi.org/10.1016/j.apm.2011.11.022</u>
- [26] Wilke, C. R., and Pin Chang. "Correlation of diffusion coefficients in dilute solutions." AIChE Journal 1, no. 2 (1955): 264-270. <u>https://doi.org/10.1002/aic.690010222</u>

- [27] Loosemore, M. J., and A. P. Prosser. "Mass transfer in a stirred vessel extractor." Chemical Engineering Science 18, no. 8 (1963): 555-556. <u>https://doi.org/10.1016/0009-2509(63)85017-4</u>
- [28] Reis, M. Teresa A., and Jorge M. R. Carvalho. "Modelling of zinc extraction from sulphate solutions with bis (2ethylhexyl) thiophosphoric acid by emulsion liquid membranes." *Journal of Membrane Science* 237, no. 1-2 (2004): 97-107. <u>https://doi.org/10.1016/j.memsci.2004.02.025</u>
- [29] Kargari, Ali, Tahereh Kaghazchi, and Mansoureh Soleimani. "Mathematical modeling of emulsion liquid membrane pertraction of gold (III) from aqueous solutions." *Journal of Membrane Science* 279, no. 1-2 (2006): 380-388. <u>https://doi.org/10.1016/j.memsci.2005.12.026</u>
- [30] Snow, Mathew, and Jessica Ward. "Fundamental distribution coefficient data and separations using eichrom extraction chromatographic resins." *Journal of Chromatography A* 1620 (2020): 460833. <u>https://doi.org/10.1016/j.chroma.2019.460833</u>
- [31] Mohammed, Ahmed A., and Noor Q. Jaber. "Stability and performance studies of emulsion liquid membrane on pesticides removal using mixture of Fe3O4Â nanoparticles and span80." *Environmental Advances* 9 (2022): 100294. <u>https://doi.org/10.1016/j.envadv.2022.100294</u>
- [32] Abd Khalil, A. T., M. M. H. Shah Buddin, N. F. Mokhtar, and S. W. Puasa. "Performance evaluation of emulsion liquid membrane for simultaneous copper and cadmium removal: dispersion tool comparison." In *IOP Conference Series: Earth and Environmental Science*, vol. 616, no. 1, p. 012077. IOP Publishing, 2020. <u>https://doi.org/10.1088/1755-1315/616/1/012077</u>
- [33] Ardehali, Babak Arabi, Parisa Zaheri, and Taher Yousefi. "The effect of operational conditions on the stability and efficiency of an emulsion liquid membrane system for removal of uranium." *Progress in Nuclear Energy* 130 (2020): 103532. <u>https://doi.org/10.1016/j.pnucene.2020.103532</u>
- [34] Ahmad, A. L., M. M. H. Shah Buddin, B. S. Ooi, and Adhi Kusumastuti. "Utilization of environmentally benign emulsion liquid membrane (ELM) for cadmium extraction from aqueous solution." *Journal of Water Process Engineering* 15 (2017): 26-30. <u>https://doi.org/10.1016/j.jwpe.2016.05.010</u>
- [35] Benderrag, Abdelkader, Boumediene Haddou, Mortada Daaou, Houaria Benkhedja, Boumedienne Bounaceur, and Mostefa Kameche. "Experimental and modeling studies on Cd(II) ions extraction by emulsion liquid membrane using Triton X-100 as biodegradable surfactant." *Journal of Environmental Chemical Engineering* 7, no. 3 (2019): 103166. <u>https://doi.org/10.1016/j.jece.2019.103166</u>
- [36] Sujatha, S., N. Rajamohan, S. Anbazhagan, M. Vanithasri, and M. Rajasimman. "Parameter screening, optimization and artificial neural network modeling of cadmium extraction from aqueous solution using green emulsion liquid membrane." *Environmental Technology & Innovation* 25 (2022): 102138. <u>https://doi.org/10.1016/j.eti.2021.102138</u>
- [37] Davoodi-Nasab, Payman, Ahmad Rahbar-Kelishami, Jaber Safdari, and Hossein Abolghasemi. "Evaluation of the emulsion liquid membrane performance on the removal of gadolinium from acidic solutions." *Journal of Molecular Liquids* 262 (2018): 97-103. <u>https://doi.org/10.1016/j.molliq.2018.04.062</u>
- [38] Kohli, Himanshu P., Smita Gupta, and Mousumi Chakraborty. "Extraction of Ethylparaben by emulsion liquid membrane: Statistical analysis of operating parameters." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 539 (2018): 371-381. https://doi.org/10.1016/j.colsurfa.2017.12.002
- [39] Malik, Maqsood Ahmad, Mohd Ali Hashim, and Firdosa Nabi. "Extraction of metal ions by ELM separation technology." Journal of Dispersion Science and Technology 33, no. 3 (2012): 346-356. <u>https://doi.org/10.1080/01932691.2011.567148</u>
- [40] Chaouchi, Sarah, and Oualid Hamdaoui. "Removal of 4-nitrophenol from water by emulsion liquid membrane." *Desalination* and Water Treatment 57, no. 12 (2016): 5253-5257. <u>https://doi.org/10.1080/19443994.2015.1021104</u>
- [41] Lakhe, Minal, Sohan A. Parbat, Bharat A. Bhanvase, and Shirish H. Sonawane. "Enhanced performance of emulsion liquid membrane prepared with aid of hydrodynamic cavitation for effective removal of Pb (II) from aqueous feed phase: Optimization using Artificial Neutral Networks modeling." *Journal of Environmental Chemical Engineering* 9, no. 6 (2021): 106866. <u>https://doi.org/10.1016/j.jece.2021.106866</u>
- [42] Datta, S., P. K. Bhattacharya, and N. Verma. "Removal of aniline from aqueous solution in a mixed flow reactor using emulsion liquid membrane." *Journal of Membrane Science* 226, no. 1-2 (2003): 185-201. <u>https://doi.org/10.1016/j.memsci.2003.09.003</u>