

Review

Emulsion liquid membrane extraction of zinc by a hollow-fiber contactor

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Abstract

Emulsion liquid membranes (ELMs) can contribute to process intensification of zinc extraction, by significantly reducing the solvent and carrier requirements in comparison with conventional solvent extraction. Di(2-ethylhexyl)phosphoric acid (D2EHPA) was used as a highly selective carrier for the transport of zinc ions through the emulsified liquid membrane. The hollow-fiber extractor appears to offer significant advantages over conventional liquid–liquid contactors for this separation because emulsion leakage and swell are practically eliminated even when treating high concentration feeds. Various hydrodynamic and chemical parameters, such as variation in feed pH; zinc concentration in feed; variation in concentrations of D2EHPA; variation in feed/emulsion volume ratios and variation in feed and emulsion flow rates, were investigated. The content of sulfuric acid as an internal did not show in the studied range any significant influence on zinc extraction through the ELM, although a minimum hydrogen ion concentration is suggested in the internal aqueous solution to ensure acidity gradient between both aqueous phases to promote the permeation of zinc ions toward the internal phase. The experimental mass-transfer coefficients have shown a stronger dependence on hydrodynamic conditions in both the external feed phase and emulsion among the parameters studied. For emulsion flow rate, mass-transfer coefficient increased from 16.3×10^{-6} m/s at 200 ml/min to 31.2×10^{-6} m/s at 640 ml/min. Significant increasing in mass-transfer coefficient observed with increasing aqueous flow rate from 9.7×10^{-6} m/s at 170 ml/min to 37.2×10^{-6} m/s at 740 ml/min. The overall mass-transfer coefficient increases from 12×10^{-6} m/s at 2% D2EHPA to 28×10^{-6} m/s at 8% D2EHPA. This means that this process is chemically controlled and the interfacial resistance has a more significant role in the extraction of zinc by emulsion liquid membrane through hollow-fiber contactor. From the results obtained, it seems that the diffusion processes in aqueous feed phase and the membrane phase have the same importance as the chemical process.

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Keywords: Emulsion liquid membrane; Hollow fiber; Zinc; Extraction; D2EHPA

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1. Introduction

Emulsion liquid membrane process (ELM) is a separation process, offer three advantages over conventional polymeric membranes: (1) relatively low-energy consumption when compared to other separation processes such as thermal evaporation, electro dialysis and pressure-driven membrane processes [1], (2) high efficiency due to large surface area available for mass transfer [2], and (3) high selectivity when carrier agents are used in the membrane phase that bind with target compounds [2].

ELM is known to be one of the most effective methods for separation and concentration when the material being extracted is present in very low concentration. As a result, the ELM has been considered a promising alternative technology for diverse separation processes including removal and recovery of various heavy metals such as copper, zinc, nickel, cadmium [3–8], uranium from different media [9–11], acids and bases [12,13], and pharmaceutical separations [2,14,15]. The ELM has also received special interest for the treatment of industrial wastewaters containing a wide range of toxic contaminants such as phenol, chlorophenol, and nitrophenol [16–20].

ELM contains a three-phase dispersion system, which consists of a stripping phase encapsulated by a membrane phase (organic phase), which in turn contains the extractant in organic diluents together with a surfactant to stabilize the emulsion droplet. Thus ELM process involves simultaneous extraction and stripping in one step. The metallic element present in lean solution forms a complex with the extractant at the interface of the emulsion globule and the feed phase. The complex formed is then shuttled through the organic phase to the organic phase-stripping phase interface from where it is stripped into the bulk of the encapsulated stripping phase [21].

In ELM, mass transfer surface area to volume ratio is very high ($1000\text{--}3000\text{ m}^2/\text{m}^3$) and internal surface area to volume ratio is still larger (typically $106\text{ m}^2/\text{m}^3$) [22]. Attempts have been made in the past research works on membrane stability, to simultaneously achieve stability, highly selective permeability and ease of demulsifications. Due to difficulty in simultaneous achievement of these properties, tradeoffs among such properties have been suggested as the solutions in proper membrane formulations.

Unfortunately, widespread use of the ELM processes has been limited due to poor stability of emulsion globules against fluid shear. Breakup of emulsions and subsequent release of the internal receptor phase to the external donor phase would nullify the extraction process. Poor stability means membrane rupture and leakage. Leakage results in spilling of the entire internal phase into the external continuous phase thereby defeating the very purpose of the liquid membrane-based process. Leakage as a serious problem in liquid membrane-based processes has been pointed out by many researchers [23–25]. High selec-

tive permeability means faster mass transfer and separation of the components. When the separated solute of interest is to be recovered and the membrane phase material is to be recycled on breaking the emulsion, ease of demulsification becomes the third most significant property of emulsion liquid membranes.

For improving the stability of ELMs, several studies attempt to enhance emulsion stability. Some of these studies used high surfactant concentration [26] and employing highly viscous oil as membrane phase [10,27,28]. Other studies investigated operational conditions optimization such as stirring speed, composition of emulsion and temperature [29–31]. Other solutions were recently proposed by conversion of the membrane phase into a suitable non-Newtonian form (i.e., pseudo-plastic) by dissolving high molecular weight polymers such as poly isobutylene [28,32] and using a Taylor vortex column as a contacting device instead of conventional mixing reactors [33,34]. Combination of the last two modifications has been proven for the extraction of a benzoic acid [34], phenol and substituted phenols [35] from a model industrial wastewater.

Dispersion free hollow-fiber contactor (HFC) can be used for ELM process. This arrangement combines the advantages of ELM as an extraction and stripping in one step and non-dispersive HFC. This will reduce the leakage of internal phase into the external aqueous phase in the absence of high shear rate in stirred contactor. Also, swelling of the internal phase can be minimized. This is due to, the pores are of the order of $0.05\text{ }\mu\text{m}$ in diameter, and the internal-phase drops are of the order of $1\text{--}10\text{ }\mu\text{m}$ in the emulsion. It is unlikely that the internal droplets of the emulsion will be present in the membrane pores.

A novel extraction technique using an emulsion liquid membrane within a hollow-fiber contactor was developed and utilized to extract copper using LIX 84 extractant [36]. Stability of the liquid membrane is not crucial when used in hollow-fiber contactors; the surfactant in liquid membrane can be reduced or even eliminated without severely impairing the performance. In total-recycle mode experiments, it was shown that the ELM can successfully extract metal even at very low feed concentration. Stability of the ELM is not crucial in HFC configurations because hollow fibers physically prevent the mixing of the feed phase and the extracting phase.

Emulsion extractions of mercury, copper and nickel from aqueous streams were studied in a hollow-fiber contactor [37]. Successful extractions of nickel and mercury have also been carried out in these extractors, 99% extraction of nickel and 96% extraction of mercury were achieved within 1 h of operation. Stirred tank extractions of these metals result in swollen emulsions containing up to 45 wt.% water from an initial of 11–15 wt.% water content.

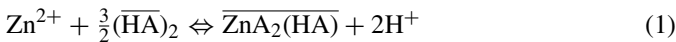
The removal of phenol from aqueous solutions using emulsion liquid membranes in a microporous hollow-fiber extractor was investigated [38]. The hollow-fiber extractor appeared to

offer significant advantages over conventional liquid–liquid contactors for this separation because emulsion leakage and swell are practically eliminated even when treating high phenolic feeds. The overall mass-transfer coefficients are seen to be more strongly dependent on the phase flow rates among the parameters studied.

The extraction of zinc from sulfuric media has experienced a renewed interest because of the use of this process on a commercial scale for treating wastewater streams and secondary materials [39]. Bis(2-ethylhexyl)phosphoric acid (D2EHPA) is the extractant mainly used in the liquid–liquid extraction of Zn^{2+} . In ELM, as in solvent extraction, organophosphorous compounds are the usual liquid ion-exchangers exchanging zinc ions for protons. The present investigations have, therefore, been undertaken to develop and characterize hollow-fiber contactors for ELM system. The present study also considered both stability and permeability of the emulsion liquid membranes. Permeability has been studied by actually using the developed emulsion liquid membrane for zinc extraction.

2. Transport of zinc in a hollow-fiber contactor using emulsion liquid membrane

Kinetics of zinc extraction for the $ZnSO_4$ –D2EHPA–isododecane system has been extensively studied [40,41]. The extraction equilibrium can be represented by the following reaction:



The extraction equilibrium constant K_{eq}^{Zn} is given by:

$$K_{eq}^{Zn} = \frac{[\overline{ZnA_2(HA)}][H^+]^2}{[Zn^{2+}][(\overline{HA})_2]^{3/2}} = m \frac{[H^+]^2}{[HA_2]^{3/2}} \quad (2)$$

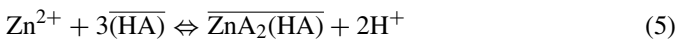
where $m = \frac{[\overline{ZnA_2(HA)}]}{[Zn^{2+}]}$.

The association equilibrium for D2EHPA is



$$K_{eq}^{HA} = \frac{[(\overline{HA})_2]}{[HA]^2} \quad (4)$$

The extraction equilibrium may be expressed by the following reaction as well:



$$K_{ex}^{Zn} = \frac{[\overline{ZnA_2(HA)}][H^+]^2}{[Zn^{2+}][\overline{HA}]^3} = m \frac{[H^+]^2}{[HA]^3} \quad (6)$$

$$K_{ex}^{Zn} = K_{eq}^{Zn}(K_{eq}^{HA})^{3/2} \quad (7)$$

The overall apparent mass-transfer coefficient can be defined by considering an overall mass balance (aqueous phase):

$$-Q_w dC_w = k_w(C_w - C_w^*) dA \quad (8)$$

where C_w^* is the solute concentration at the aqueous–organic interface. The experimental conditions used for this study were

chosen to minimize resistance in the membrane and solvent phases. Under these conditions $C_w^* \ll C_w$, leading to the simplification that $C_w - C_w^* \cong C_w$. Integrating over the module leads to Eq. (9) which enables calculation of experimental overall mass-transfer coefficients for aqueous flowing in either the shell or tube side of the module.

$$k_w = \frac{Q_w}{A} \ln \left(\frac{C_w^{in}}{C_w^{out}} \right) \quad (9)$$

Mass transfer in a hollow-fiber contactor can be described using a conventional resistance-in-series model [42]. When mass transfer is transport limited, the overall mass-transfer coefficient (k_w), for extraction of a solute from an aqueous to a solvent phase (based on aqueous in the tube side), can be represented by Eq. (10) [43]. The underlying assumption, when applying this model to describing zinc mass transfer, is that the chemical reaction described by Eq. (1) is fast and reaches equilibrium at the interface:

$$\frac{1}{k_w} = \frac{1}{k_t} + \frac{d_i}{mk_m d_{lm}} + \frac{d_i}{mk_s d_o} \quad (10)$$

where $d_{lm} = \frac{d_o - d_i}{\ln(d_o/d_i)}$.

The local mass-transfer coefficients for the boundary layer resistance in the tube side, diffusion of the solute in the membrane pores and boundary layer resistance in the shell side, are given by k_t , k_m and k_s , respectively. With the aqueous phase in the shell side, the aqueous–organic interface is on the outside surface of the lumen and Eq. (10) can be:

$$\frac{1}{K_w} = \frac{d_o}{mk_i d_i} + \frac{d_o}{mk_m d_{lm}} + \frac{1}{k_s} \quad (11)$$

Yang et al. [44] and Yang and Cussler [45] concluded the importance of the interfacial chemical reaction resistance on the interface of feed phase and organic phase. For the extraction of zinc by emulsion liquid membrane, Teresa et al. [46] noted that the interfacial reaction resistance played an important role for lower pH values for zinc extraction by emulsion liquid membrane. So, according to Yang et al. [44] and Teresa et al. [46], Eq. (10) rewrites to include the interfacial chemical reaction resistance (Eq. (12)).

$$\frac{1}{K_w} = \frac{d_i}{mk_s d_o} + \frac{d_i}{mk_m d_{lm}} + \frac{1}{k_t} + \frac{[H^+]}{\varepsilon k_f [\overline{HA}]_{FI}} \quad (12)$$

For laminar flow in the tube side of the membrane, the tube side local mass-transfer coefficient is related to the Sherwood number using the Leveque approximation [47], according to Eq. (13):

$$Sh_t = \frac{k_t d_i}{D_w} = 1.62 Sc^{1/3} Re^{1/3} \left(\frac{d_i}{L} \right)^{1/3} \quad (13)$$

In the membrane, the local mass-transfer coefficient can be calculated from known membrane parameters of solute diffusivity (D_{org}), membrane thickness (δ), tortuosity (τ) and porosity (ε), according to Eq. (14) [42]. The diffusivity is for the organic phase, D_{org} , because the membrane is hydrophobic and is wetted

by the organic.

$$k_m = \frac{D_{\text{org}} \varepsilon}{\delta \tau} \quad (14)$$

Mass transfer correlations on the shell side depend on the type of flow within the module. For cross-flow hollow-fiber modules, a significant portion of the flow is perpendicular to the lumen bundle and various approaches have been used. The conventional approach is to define the Sherwood number in terms of the outer fiber diameter, d_o , as shown in Eq. (15). The Reynolds number is also defined with d_o as the characteristic length. The superficial velocity is calculated as the flow rate through the shell divided by the cross-sectional area. Where flow in a cross-flow module is radial, the cross-sectional area varies with diameter and the arithmetic average area is used [48]. The effective velocity is then calculated as the superficial velocity divided by the void fraction.

$$Sh_s = \frac{k_s d_o}{D_s} = \alpha Sc_s^{1/3} Re_s^\beta \quad (15)$$

where α and β are shell side correlation coefficients. Schonert et al. [49] developed a modified approach to shell side correlations in cross-flow modules where the characteristic length and velocity calculations were adapted specifically for cylindrical cross-flow modules. In this case, in the calculation of the Sherwood number, the hydraulic diameter, d_h , replaced d_o , which was calculated, as per Eq. (16), and the superficial velocity was defined as the log mean average velocity, as shown in Eq. (17):

$$d_h = \frac{4 \text{ volume of voids filled with fluid}}{\text{wetted surface area of the bed}} \\ = \frac{4V_m}{A} = \frac{d_{so}^2 - d_{si}^2 - nd_{hf}^2}{nd_{hf}} \quad (16)$$

$$v_s = \frac{Q_s}{\pi(L/2)(d_{so} - d_{si})} \quad (17)$$

3. Experimental

The extractant D2EHPA from Baysolvex BAYER was used without purification. Gefachem-Prochemie, Leverkusen, supplied the high purity isododecane was used as received, as a solvent for D2EHPA. Sorbitane monooleate (span 80, Sigma-Aldrich) was used as a surfactant for emulsion formulations. The aqueous phase was prepared by dissolving $ZnSO_4 \cdot 7H_2O$, of analytical grade (Fisher Scientific) in 0.5 M sulfuric acid solutions, in which the pH was adjusted to be 0.1–4 by adding a small amount of 0.1N NaOH. The initial concentrations of metals in aqueous phase ranged from 100 to 1000 ppm and of D2EHPA in the organic phase ranged from 2 to 8 vol.%, respectively. The internal phase consisted of 0.5–2 M sulfuric acid. The organic phase was prepared by dissolving D2EHPA in isododecane and appropriate amount of span 80 as a surfactant then added. The emulsion was prepared by mixing the internal aqueous solution with the organic membrane phase using a rotor-stator type high-speed disperser (IKA Ultra Turrax T50)

Table 1
Geometric characteristics of the tested hollow-fiber contactor

Provider	Hoechst Celanese Corporation
Contactor type	Celgard X-30 Microporous Polypropylene Hollow Fiber [Liqui-Cel Extra-Flow 2.5 in. × 8 in. (64 mm × 203 mm)]
Shell diameter (cm)	6.3
Fiber bundle diameter (cm)	4.7
Distribution tube diameter (cm)	2.2
Effective surface area (m ²)	1.4
Effective fiber length (cm)	15
Effective area/volume (cm ² /cm ³)	29.3
Number of fibers	9950
Outer fiber diameter (μm)	300
Inner fiber diameter (μm)	240
Fiber wall thickness (μm)	30
Fiber porosity	0.4
Pore tortuosity	2.25
Effective pore diameter (μm)	0.03

at 1047 rad/s (10,000 rpm). The mixing time was 300 s. A predetermined volume ratio of 1:1 was maintained for organic phase to the internal stripping phase. The emulsion volume was 11 and the external aqueous phase volume is 41. During extraction, samples were periodically taken through plastic syringe with 3 ml volume. After permeation the emulsion volume was measured. The concentration of solute, in the external aqueous phase, was measured with a Hitachi Z8100 atomic absorption spectrophotometer. The pH value of the external phase was measured before and after each run on a Metrohm 632 pH meter. The influence of surfactant on the mass transfer was obtained by applying the membrane phase (with 2–8 vol.% of surfactant). The viscosity of the emulsions was measured using a Brookfield DV-II+ programmable viscometer at different shear rates. Interfacial tension data were obtained with a LAUDA TVT1 tensiometer.

Emulsion liquid membrane using hollow-fiber contactor experiments were conducted using the Liqui-Cel Extra-Flow 2.5 cm × 8 cm membrane contactor (Model G261; Hoechst Celanese). Table 1 provides all information about this module. Fig. 1 shows a detailed schematic of the module, which is actually the baffled one where the shell side fluid flows perpendicular to the fibers. As the membrane material was hydrophobic, the pores were filled with the emulsion. In this case, a MCP-Z pump and flows through the shell side delivered emulsion. Aqueous phase, delivered by a MCP-Z pump in total-recycle mode, flows

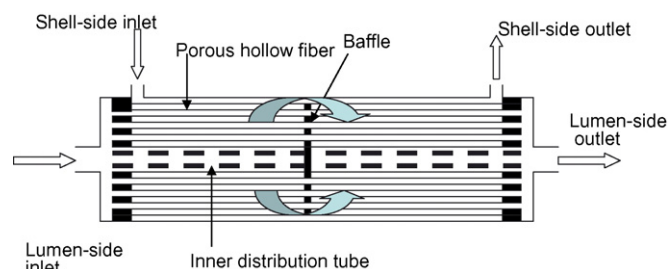


Fig. 1. Liquicel extra-flow hollow-fiber contactor.

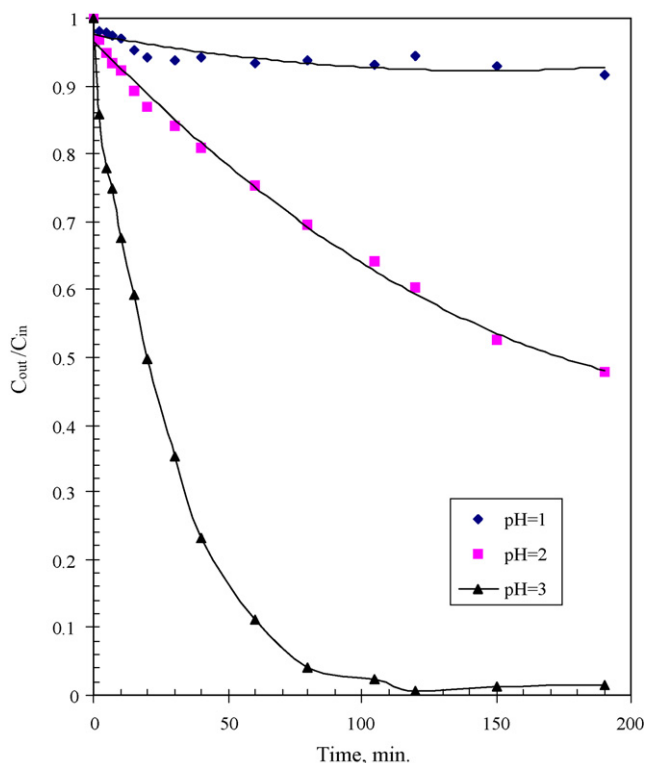


Fig. 2. C_{out}/C_{in} vs. time as a function of acidity of the external phase.

through the tube side of the hollow-fiber module. To prevent the organic phase from flowing out of the membrane pores and mixing with the aqueous phase, a higher pressure is applied to the aqueous side. The pressure regulators control the pressure of the system and the flow rate is adjusted automatically by the flow meter at the inlet of the module.

4. Results and discussions

4.1. Effect of the acidity of the feed solutions

The effect of the bulk hydrogen concentration in the feed solution on the extraction of zinc is shown in Fig. 2. From this figure, it is observed that at lower hydrogen ion concentrations the extraction of zinc increases sharply because the formation of the zinc-carrier complex at the interface between the feed and liquid membrane is favored according to the equilibrium relationship. However, when the hydrogen concentration increases, it is seen that zinc extraction is limited. This limitation can easily be understood considering the acidic carrier at the interface between the feed solution and liquid membrane. In a real system, higher pH is not a good operation condition because zinc hydroxide precipitates begin to form.

Fig. 3 shows the effect of feed solutions acidity on the overall mass-transfer coefficient. It is concluded that with decreasing the feed solutions acidity, the overall mass-transfer coefficient increased sharply. This was observed for pH 3 feed solution; k_w reached 32×10^{-6} m/s. When the pH of the external phase decreases, the kinetics will be lower and the resistance of mass transfer in the external phase will be less important. On the

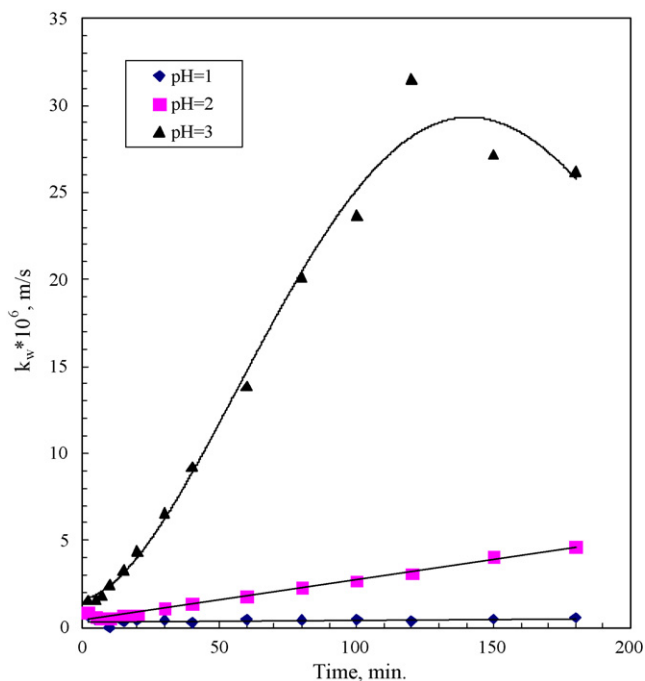


Fig. 3. Overall mass-transfer coefficient vs. time as a function of acidity of the external phase.

other hand, the resistance due to diffusion goes down for lower pH values, which means that the rate of zinc complex formation becomes the rate-determining step under this condition. It will be expected that the transport of zinc in the external phase and the diffusion in the globule will be the rate-determining steps at higher pH values.

4.2. Effect of initial zinc concentration

The influence of the initial concentration of zinc in the external phase on the extraction rate is shown in Fig. 4. It is observed that the degree of extraction decreases when the initial content of zinc increases. At low zinc concentration (100–700 ppm), zinc level in the feed solutions decreased to about 2% of the initial value. But at 1000 ppm solutions, zinc extraction reaches about 90%.

On the other hand, the variation of the overall mass-transfer coefficient was calculated and plotted against initial zinc concentration in Fig. 5. The concentration dependence of the overall mass-transfer coefficient can be interpreted by Eq. (12), in which the distribution coefficient (m) is in the denominator of two resistances in the solvent phase. However, the distribution coefficient is concentration dependent. Thus, the value of the overall resistance is increasing and the value of k_w is decreasing with decreasing distribution coefficient (m).

The increasing of k_w was attained as the initial zinc concentration increased at any instant of time. This is due to the increasing in the concentration polarization in the liquid boundary layer. Another aspect, the saturation of the internal droplets of the emulsion is attained more rapidly for high concentrations in the external phase. When the solute concentration is high, the zinc complex must diffuse through the membrane phase to

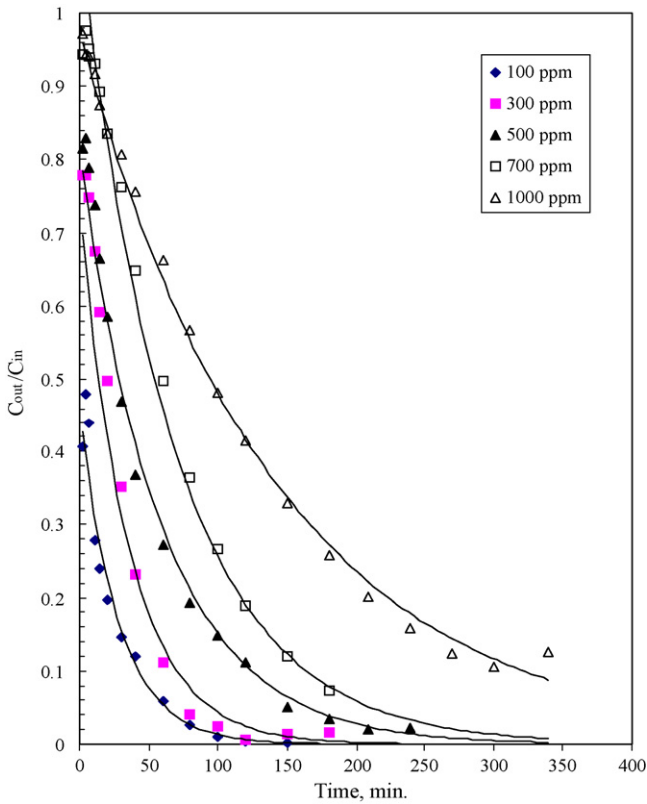


Fig. 4. C_{out}/C_{in} vs. time as a function of initial Zn concentration in aqueous phase.

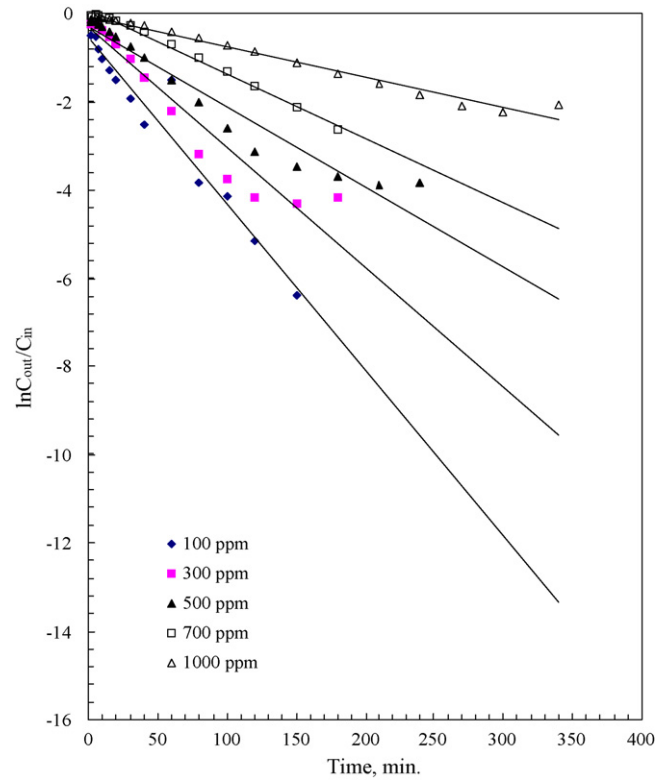


Fig. 6. $\ln C_{out}/C_{in}$ vs. time as a function of initial Zn concentration in aqueous phase.

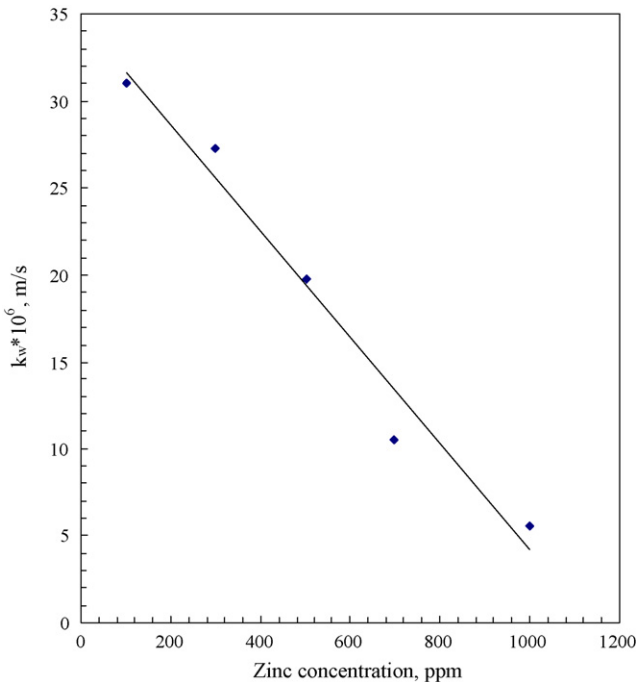


Fig. 5. Effect of initial zinc concentration in external phase on the overall mass-transfer coefficient.

the internal phase. This suggests that the mass transfer resistance in the emulsion globule is important. A similar behavior was reported by other authors [46,50]. Great dependence of the k_w on the initial concentration was achieved. By plotting $\ln C_{out}/C_{in}$ versus time (Fig. 6), we concluded that the mass transfer of zinc is a first-order process. This means that the resistances of the interfacial reaction and the membrane must be more important.

4.3. Effect of carrier concentration

The effect of carrier concentration on zinc extraction is shown in Fig. 7. At a fixed sulfuric acid concentration in the internal aqueous phase, a noticeable increase from 78 to 99% in zinc extraction with an increase in the carrier concentration to 6% was observed. It is conceivable that the increase of the carrier concentration in the membrane phase and hence at the membrane–external aqueous interface enhances the formation of zinc–carrier complexes, resulting in increasing diffusion of zinc from the external aqueous phase to the membrane surface, and the formed complexes through the membrane to the internal aqueous phase. A further increase in the carrier concentration (from 6 to 8%) showed a slight increase in the zinc extraction to the internal aqueous phase was observed. It is evident from Fig. 8 that the carrier concentration has a significant effect on the recovery of zinc from aqueous sulfuric acid solutions. The overall mass-transfer coefficient increases from 12×10^{-6} m/s at 2% D2EHPA to 28×10^{-6} m/s at 8% D2EHPA. This means that this

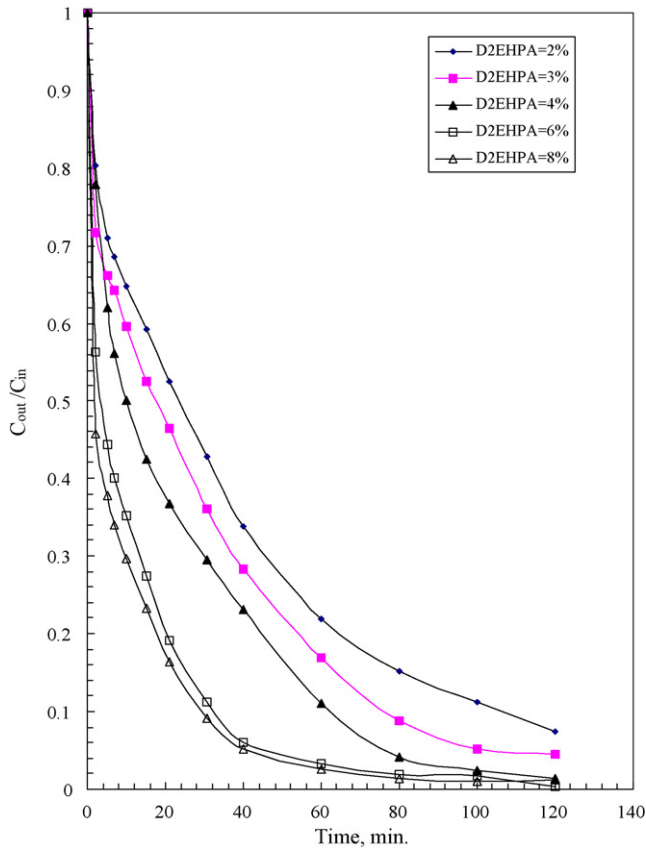


Fig. 7. C_{out}/C_{in} vs. time as a function of D2EHPA concentration.

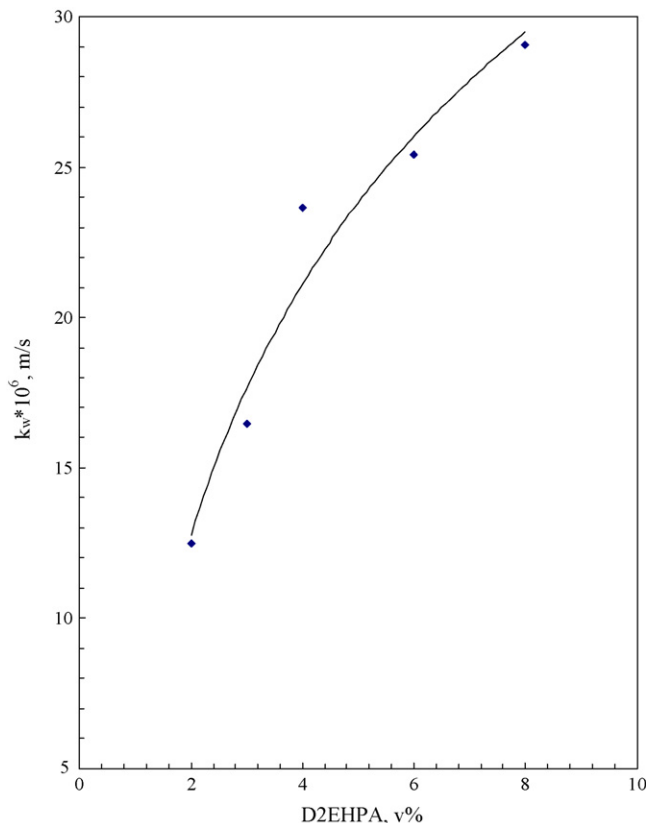


Fig. 8. Effect of D2EHPA concentration on the overall mass-transfer coefficient of zinc.

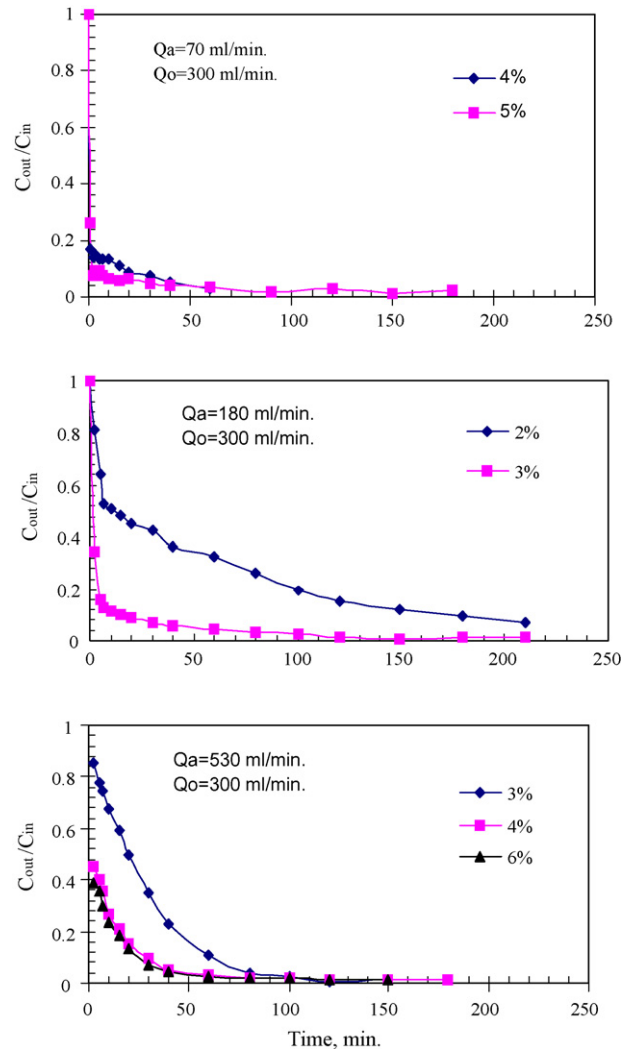


Fig. 9. C_{out}/C_{in} vs. time as a function of span 80 concentration.

process is chemically controlled and the interfacial resistance has a more significant role in the extraction of zinc by emulsion liquid membrane through hollow-fiber contactor.

4.4. Influence of surfactant concentration

Stability of ELM depends mostly on the surfactant concentration. Fig. 9 compares ELM extraction in an HFC with varying surfactant concentrations. This figure implies that the extraction of zinc increases as the span 80 concentration increases. This was observed with different surfactant concentrations at different aqueous flow rates. This is due to the increasing in the emulsion stability as the surfactant concentration increased. On the other hand, the effect of a surfactant concentration on the overall mass-transfer coefficient is plotted in Fig. 10. Mass-transfer coefficient increases as the surfactant increase. We observed that no swelling occurred in the emulsion volume after 4 h extraction cycle. Although the emulsion viscosity increases with increasing surfactant concentration, the mass-transfer coefficient increased.

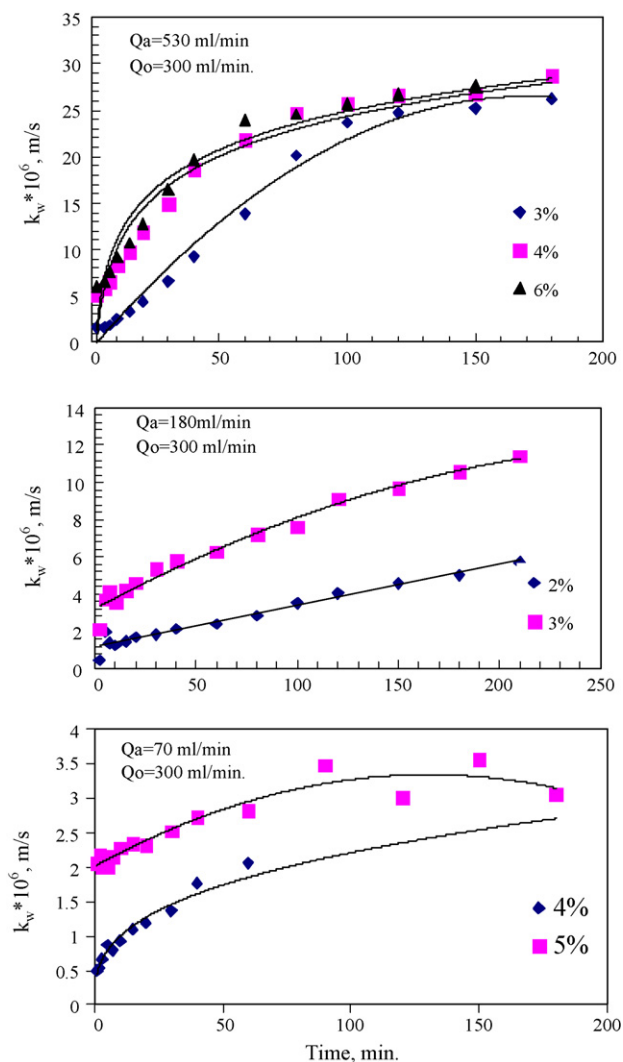


Fig. 10. Effect of span 80 concentration on the overall mass-transfer coefficient.

4.5. Effect of internal-phase concentration

The role of internal phase in zinc extraction is studied in the concentration range from 0.5 to 2.5 M H_2SO_4 and the data obtained is illustrated in Fig. 11. As shown in this figure, after 120 min. Cycle time C_{out}/C_{in} changed from 0.035 at 0.5 M to 0.034 at 2.5 M. These values means that the final zinc ion concentration in the aqueous phase are nearly the same for different sulfuric acid concentrations and a slight increase of zinc transfer with increasing sulfuric acid concentration was observed. The difference of hydrogen ion chemical potentials between the two aqueous phases is the main driving force in the ELM process. It was expected that increasing the amount of H_2SO_4 in the internal phase decreased the difference of densities and increased the emulsion viscosity. The increasing of emulsion viscosity reflected in an increasing in the size of drops. Another point to be reported is the concentration of zinc in the receiving phase. In all experiments, essentially no emulsion swell was observed.

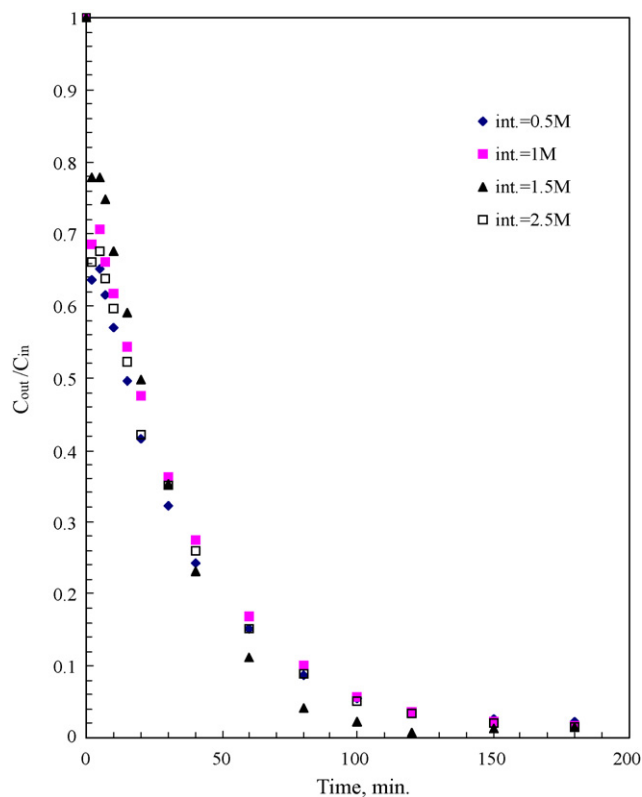


Fig. 11. C_{out}/C_{in} vs. time as a function of internal-phase concentration.

4.6. Effect of external/emulsion phase ratio

It is known that the volume ratio of the W/O emulsion to the external aqueous solution controls interfacial mass transfer across ELMs. The influence of external to emulsion volume ratio in the range from 4/1 to 15/1, on the extraction of zinc is illustrated in Fig. 12 shows that over the ratio values examined, increasing ratio caused a decrease in zinc ion transfer. The effect of the ratio appears for the cycle time up to 100 min, after that time (175 min) the same extraction rate was observed.

The effect of the ratio on the mass-transfer coefficient was illustrated in Fig. 13. By inspection of this figure, we observed that increasing the ratio has a negative effect on k_w . At an aqueous to emulsion ratio 4, k_w is 31×10^{-6} m/s whereas at 15 reached 21×10^{-6} m/s.

4.7. Effect of aqueous flow rate in the tube side

The extraction rate of zinc at various flow rates of the feed solution is shown in Fig. 14. This figure shows the variation of zinc concentration in feed solution with time. As time increases, zinc ions are depleted in the feed solution. The depletion of zinc induces the formation of zinc-carrier complexes, resulting in the increase of the zinc extraction rate. The extraction rate of zinc becomes higher as feed flow rate increases. The extraction rate increases since the increase of flow rate reduces the mass-transfer resistance in the liquid boundary layer. But the extraction rate of zinc is determined by the mass-transfer coefficient in the liquid membrane at higher flow rate where

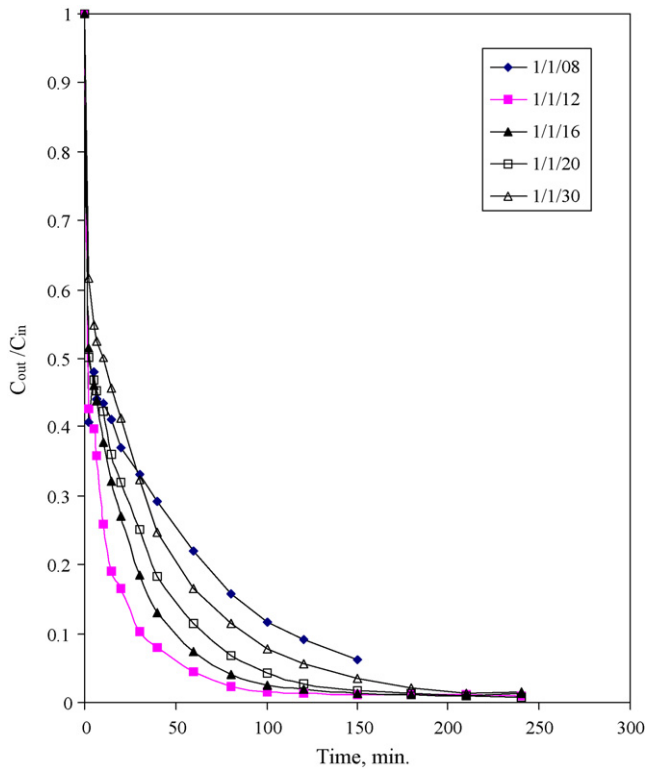


Fig. 12. C_{out}/C_{in} vs. time as a function of internal/organic/external phase ratio.

mass-transfer coefficient in the feed solution is much higher than that in the liquid membrane.

The dependences of the overall mass-transfer coefficient on the feed flow rate, with a constant feed concentration are pre-

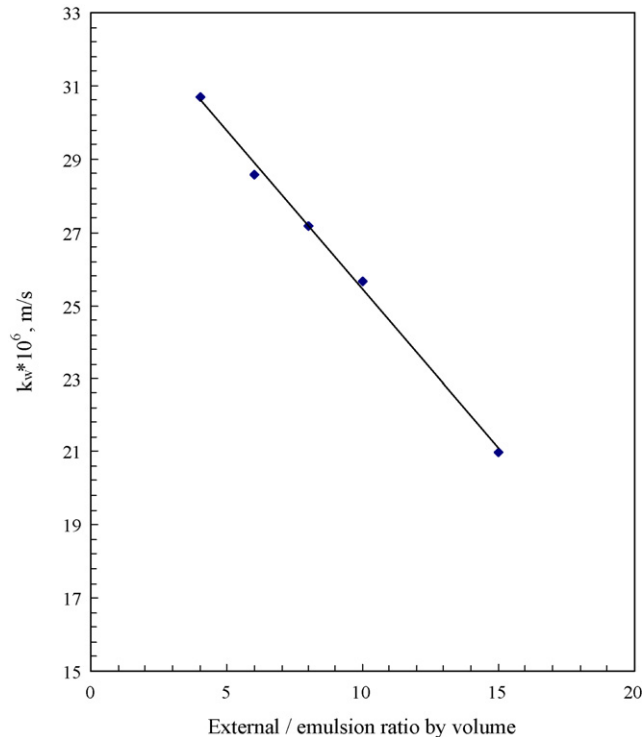


Fig. 13. Effect of external/emulsion phase ratio on zinc overall mass-transfer coefficient.

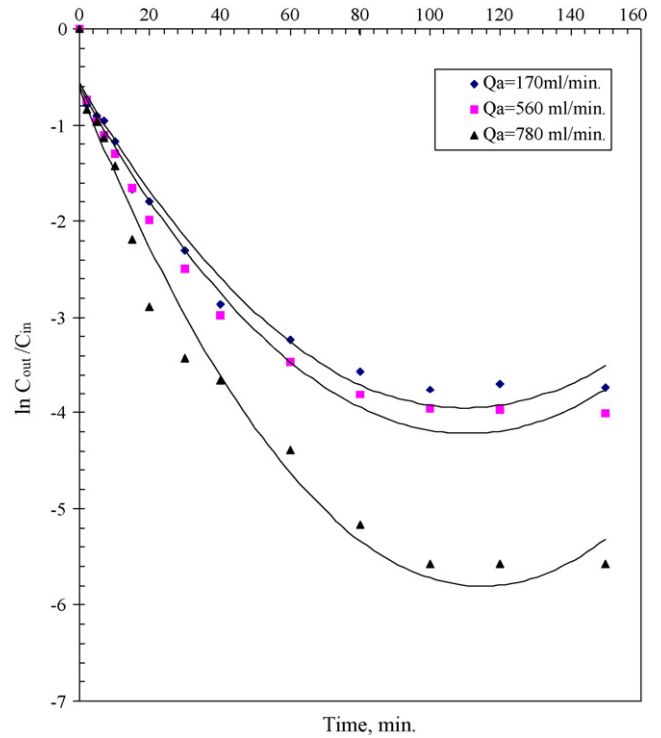


Fig. 14. $\ln C_{out}/C_{in}$ vs. time as a function of aqueous flow rate.

sented in Fig. 15. When considering the mass-transfer data shown in Figs. 15 and 16, the value of the overall mass-transfer coefficient is more dependent of the feed flow rate. Varying the flow rate of the aqueous feed affects the mass-transfer coefficient to a much larger extent, with k_w increasing from 9×10^{-6}

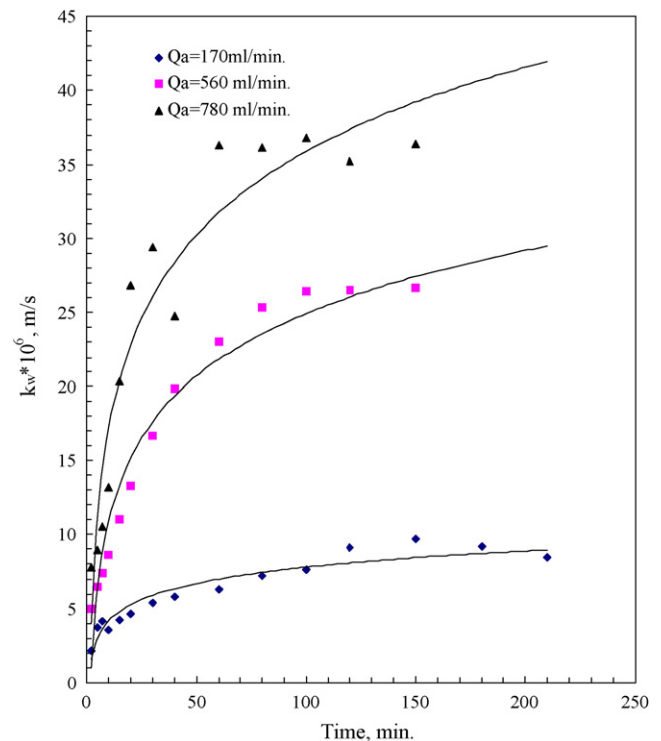


Fig. 15. Overall mass-transfer coefficient as a function of aqueous flow rate.

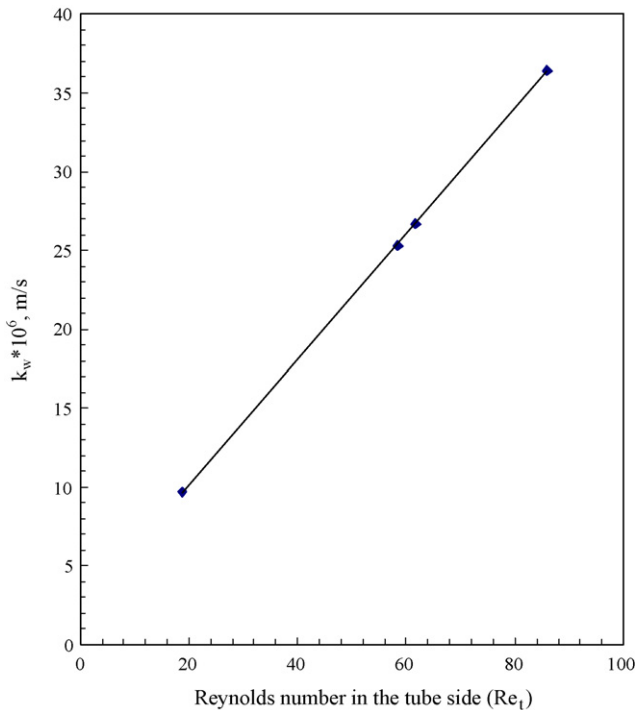


Fig. 16. Tube-side mass-transfer coefficient vs. Reynolds number (Re_t) in the tube side as a function of the aqueous flow rate with constant flow rate of emulsion phase.

to 37.2×10^{-6} m/s. This points to the importance of resistances in the aqueous boundary layer in this contactor.

4.8. Effect of emulsion flow rate

In order to investigate the effect of emulsion flow rate on zinc extraction, a set of experiments was carried out at very small Re_s in the shell side. An increase in the flow rate of emulsion significantly increases the zinc extraction rate and reduces zinc concentration in the aqueous outlet solution (Fig. 17), implying that the organic boundary layer resistance plays an important role in the zinc extraction rate. The great influence of emulsion flow rate on its saturation is evident by proper adjustment of Re . It is possible to obtain more than one order of magnitude increase of solvent saturation.

An increase in the aqueous feed flow rate increases the zinc extraction rate and the mass-transfer coefficient k_w substantially (Fig. 16), implying the aqueous boundary layer resistance is an important contributor to the total mass-transfer resistance. However, its effect on the zinc extraction rate is not as strong as that of the flow rate of emulsion (Fig. 18). Indeed, with decreasing Re_s , the relative contribution of resistance in the shell is increasing.

Finally, it is important to stress the role played by the emulsion flow rate (in the shell) in the overall membrane-based extraction process. Indeed, the flow rate in the lumen and Re_s is shown to be a very significant parameter of the overall process. More precisely, it determines the degree of solvent saturation, which is one of the main parameters to assess extraction process performance. Therefore, emulsion flow rate and the respective

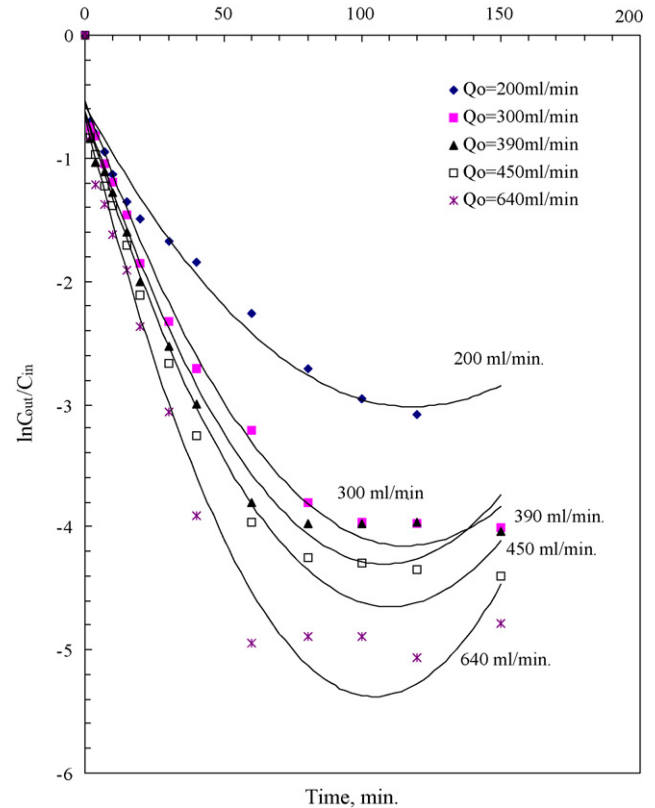


Fig. 17. $\ln C_{out}/C_{in}$ vs. time as a function of emulsion flow rate.

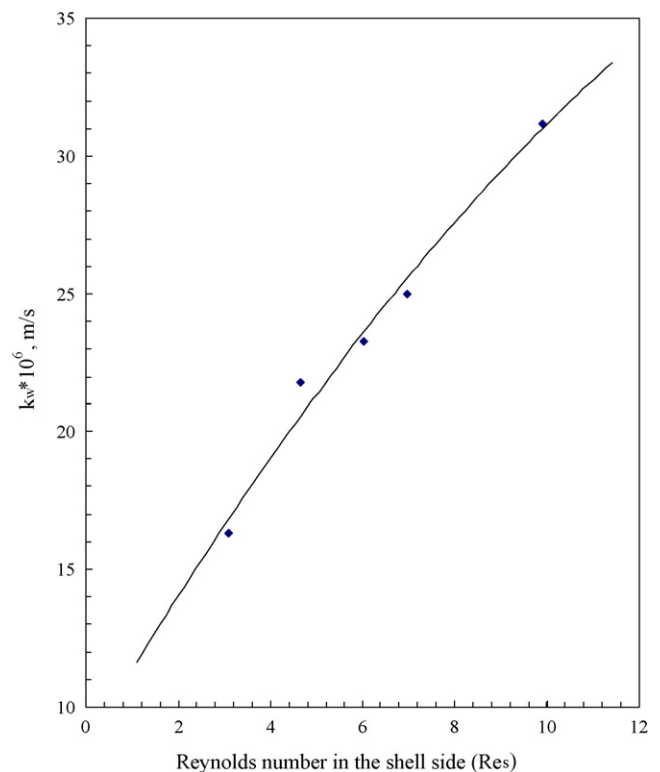


Fig. 18. Tube-side mass-transfer coefficient vs. Reynolds number in the shell side (Re_s) as a function of emulsion flow rate with constant flow rate of aqueous phase.

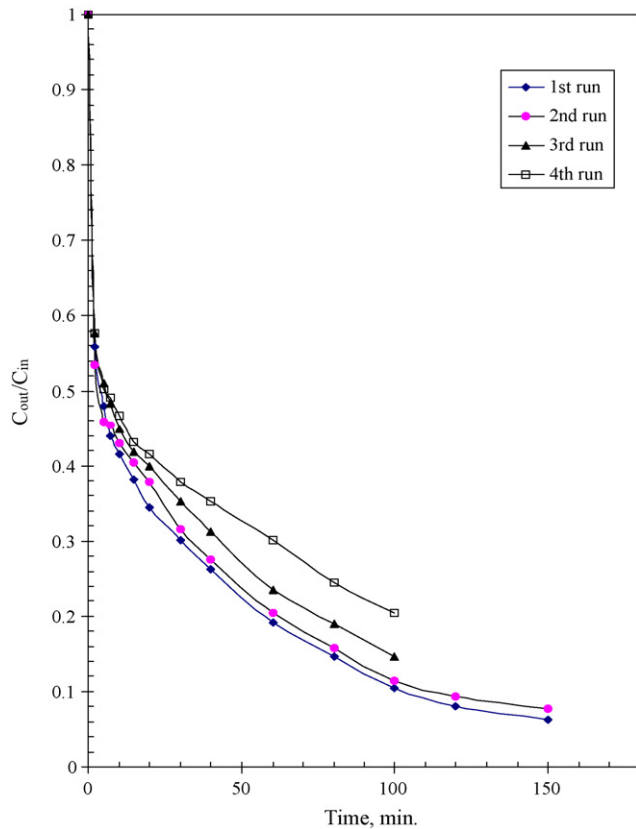


Fig. 19. C_{out}/C_{in} vs. time for emulsion saturation.

Reynolds number Re_s should be properly taken into account in designing the extraction process.

4.9. Emulsion saturation

The concentration-versus-time data for extraction of zinc from aqueous solution in a hollow-fiber membrane module with an emulsion containing 4-vol.% D2EHPA-isododecane, 3-vol.% span 80 solutions are shown in Fig. 19. The results are shown for four replicate runs at 300 and 530 ml/min shell side (emulsion) and tube side (aqueous feed) flow rates, respectively. After 100 min cycle time the extraction rate reaches 90, 89, 85.5, and 79.5 for 1st, 2nd, 3rd and 4th run, respectively. Emulsion was stable during these runs and there is no swelling of the emulsion observed.

5. Conclusions

Utilization of hollow-fiber contactors for emulsion liquid membrane has the advantages of ELM with eliminating encountered problems in high shear contactors, such as swelling and leakage of the liquid membrane. This technique is a promising alternative to conventional methods and should increase awareness of the potential for recovery of heavy metal ions. Results show the feasibility of the removal and/or recovery of zinc from dilute aqueous solutions using this contactor based on a surfactant liquid membrane.

A remarkable degree of zinc enrichment in the receiving phase can be achieved by reducing the volume ratio between the strip acceptor phase and the external feed solution. The D2EHPA extractant plays a fundamental role in the process as metal-carrier although it has a lower interfacial activity than the surfactant. The surfactant stabilizes the emulsion by reducing the interfacial tension and avoiding the coalescence of droplets. However, it is not recommended to use an excess of surfactant in the membrane because it would compete with the extractant molecules for the sorption of active sites on the interface, increasing the interfacial resistance and lowering the efficiency of the metal transport process. From the data obtained, it may be concluded that all three resistances, namely, the organic boundary layer resistance, the interfacial reaction resistance, and the aqueous boundary layer resistance, affect the zinc extraction rate and the mass-transfer coefficient; further the organic boundary layer resistance plays a key role in the zinc extraction rate in the HFM extractor.

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Nomenclature

A	membrane area at the interphase (m^2)
C	solute concentration (mol/m^3)
d_i	internal membrane diameter (m)
d_o	outer membrane diameter (m)
d_{hf}	hollow-fiber diameter (m)
d_{lm}	log mean diameter (m)
D	diffusivity (m^2/s)
$[H^+]$	concentration of hydrogen ion in the aqueous phase (mol/m^3)
$[HA]$	concentration of free D2EHPA in the organic phase (mol/m^3)
$[(HA)_2]$	dimeric concentration of free D2EHPA (mol/m^3)
J	flux ($mol/m^2 s$)
k	mass-transfer coefficient (m/s)
K_{eq}^{Zn}	equilibrium constant for zinc
K_{eq}^{HA}	dimerization constant of D2EHPA (m^3/mol)
K_{ex}^{Zn}	extraction equilibrium constant for zinc
L	length of hollow fiber (m)
m	equilibrium distribution coefficient
Q	flow rate (m^3/s)
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
V	volume (m^3)
v	velocity (m/s)
$[Zn^{2+}]$	concentration of zinc in the aqueous phase (mol/m^3)

[ZnA₂(HA)] concentration of the zinc–D2EHPA complex in the organic phase (mol/m³)
 bracket [] molar concentration (mol/m³)
 overbar organic phase

Subscripts

f forward reaction rate constant
 FI feed–emulsion interface at fiber outer diameter
 h hydraulic
 i interfacial reaction
 m membrane
 o organic
 s shell
 si inner
 so outer
 t tube
 w aqueous

Superscripts

in module inlet
 out module outlet
 * aqueous–organic interface

Greek symbols

Δ fractional resistance
 α shell side correlation coefficient
 β shell side correlation coefficient
 δ membrane thickness (m)
 ε porosity
 τ tortuosity

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