R&D NOTES

Extraction with Emulsion Liquid Membranes in a Hollow-Fiber Contactor

B. Raghuraman and J. Wiencek
Dept. of Chemical and Biochemical Engineering, Rutgers University, Piscataway, NJ 08855

Aqueous streams contaminated with heavy metal ions may be produced as effluents from industrial plants or during attempts to remediate solids loaded with heavy metals, such as contaminated soils. Metals of particular concern include copper, zinc, cadmium, nickel, mercury, lead, and chromium.

An extraction system for heavy metals recovery from dilute waste streams, which can accomplish both extraction and stripping in one step, is an emulsion liquid membrane (ELM), first invented by Li (1968). ELMs are made by forming an emulsion between two immiscible phases. Usually stabilized by surfactants, the water-in-oil emulsion contains the metal extracting agent in the oil phase and the stripper in the aqueous receiving phase. This emulsion is then dispersed by mechanical agitation into a feed phase containing the metal to be extracted. Figure 1 shows an emulsion liquid membrane extraction of mercury(II). Combining the extraction and stripping processes removes equilibrium limitations and reduces metal concentrations in the feed to very low levels. Various liquid membrane formulations have been used to extract copper, zinc, mercury, cobalt, chromium, and nickel from waste streams (Larson and Wiencek, 1992; Gu et al., 1986; Fuller and Li, 1984; Weiss and Grigoriev, 1982; Boyadzhiev and Bezenshek, 1983; Kitagawa et al., 1977; Izatt et al., 1987). Demulsification by application of high-voltage electric fields has proved to be most efficient (Draxler et al., 1988). Heavy metals concentrated in the receiving phase can be recovered by electroplating or precipitation. The oil phase can be recycled.

The ELM extraction in a stirred contactor as described above has two main disadvantages. On prolonged contact with the feed stream (greater than 10 min), the emulsion swells with water, increasing the internal-phase volume. While the aqueous content of the emulsion is typically 10–20 wt. % at the start of a separation, it has been found to contain up to 35–50 wt. % water at the end. This swelling is most likely attributed to two phenomena: (1) osmotic swelling resulting from the difference in salt content between the internal phase of the emulsion and the feed phase and (2) feed-phase entrainment. Swelling and water uptake cause: a reduction in the stripping reagent concentration in the internal phase which in turn reduces the stripping efficiency; dilution of the solute that has been concentrated in the internal phase resulting in lower sep-

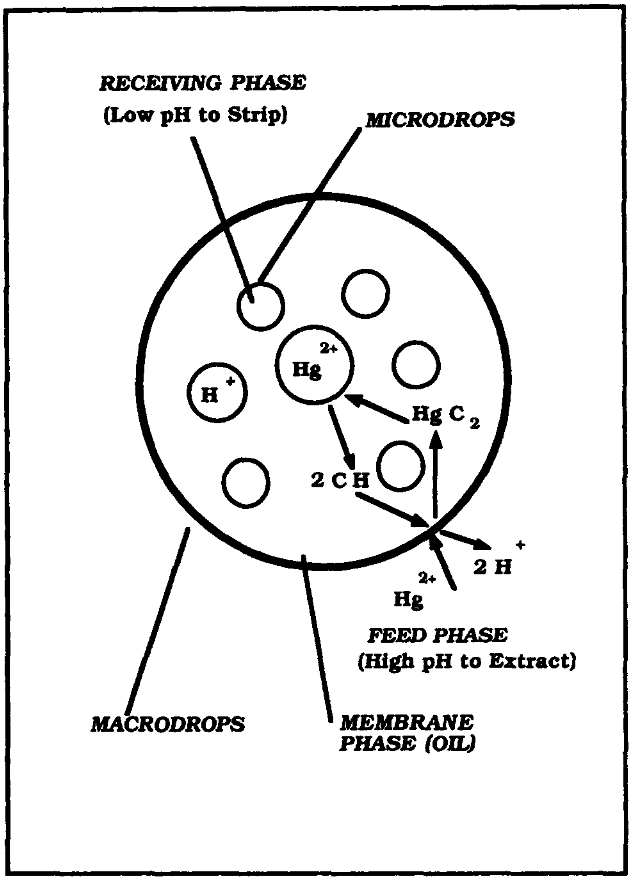


Figure 1. Mercury ion extraction with an emulsion liquid membrane.

Mercury(II) is transported to the emulsion/feed-phase interface and reacts with the complexing agent (CH) to form a soluble mercury complex (HgC_2). This complex diffuses to the interior of the emulsion droplet until it encounters a microdroplet of the internal phase where the metal ion is exchanged for a hydrogen ion. The net effect is a unidirectional mass transport of the cation from the original feed to the receiving phase with countertransport of hydrogen ions. The dispersion is then allowed to settle and the lower aqueous stream is withdrawn for discharge. The upper emulsion phase is then demulsified to split the membrane and the enriched stripping phases.

aration efficiency of the liquid membrane; a reduction in membrane stability by making the membrane thinner; and an increase in the viscosity of the spent emulsion, making it more difficult to demulsify.

The second disadvantage of ELM extractions in a stirred contactor is the leakage of the internal-phase contents into the feed stream because of membrane rupture. Leakage, like swelling, also reduces the efficiency of separation. The leakage can be minimized by making more stable emulsions with optimized surfactants, but this makes the subsequent demulsification and product recovery steps more difficult. Lower shear rates would also minimize leakage, but mass-transfer resistances could then become very significant.

This work focuses on the use of microporous hollow-fiber contactors (HFC) as an alternate contacting method to direct batch/continuous dispersion of emulsion liquid membranes. This method of contact will retain the primary advantage that emulsion liquid membrane separations offer, namely, extraction and stripping in a single processing step which circumvents the limits of equilibrium inherent in conventional solvent extraction. However, because hollow-fiber membranes, by their design, allow for high surface area contacting without the high shear rates typically encountered with an agitator, this will result in improved efficiency of extraction by reducing membrane swelling and leakage.

Solvent Extraction in Hollow-Fiber Contactors

Dispersion-free solvent extraction using microporous hollow-fiber contactors has been shown to be very effective (Alexander and Callahan, 1987; Dahuron and Cussler, 1988; Prasad and Sirkar, 1988, 1990). Hollow-fiber contactors consist of microporous hollow fibers arranged in a shell-and-tube configuration. The microporous hollow fibers can be either hydrophobic or hydrophilic. In either case, a stable interface can be maintained by keeping the nonwetting phase at a higher pressure. Consider the case where the organic phase flows through the hydrophobic fibers, while the aqueous phase flows on the shell side. The aqueous phase will not penetrate or wet the hydrophobic fiber membrane pores as the membrane is hydrophobic. The organic phase, however, will readily wet the pores and directly contact the aqueous phase. By applying a higher pressure on the aqueous phase, the interface is essentially immobilized at the pore entrances on the aqueous side. The pressure on the aqueous phase should not exceed the breakthrough pressure beyond which the aqueous phase will start penetrating the fiber membrane pores. The advantage of the hollow-fiber contactor lies in its ability to offer very high surface area/volume ratios without dispersion or mixing of the two phases. Use of hollow-fiber contactors eliminates the need for a settling stage and allows direct scale-up due to a modular design (Prasad and Sirkar, 1990).

Emulsion Liquid Membrane Extractions in Hollow-Fiber Contactors

An emulsion liquid membrane can be used to simultaneously extract and strip the metal from the wastewater (thus removing equilibrium limitations of conventional solvent extraction) by a liquid-liquid dispersion-free contacting in a hollow-fiber contactor. This combines the advantages of emulsion liquid membrane separation (simultaneous extraction and stripping) and dispersion-free solvent extraction. The absence of high shear rates, which are encountered in agitated dispersions, minimizes leakage of internal stripping phase. Figure 2 shows mercury extraction/stripping with an ELM in a hydrophobic HFC. The organic membrane readily wets the pores, but is prevented from flowing out by the higher pressure on the aqueous phase. Thus, a stable interface is maintained at the pore openings.

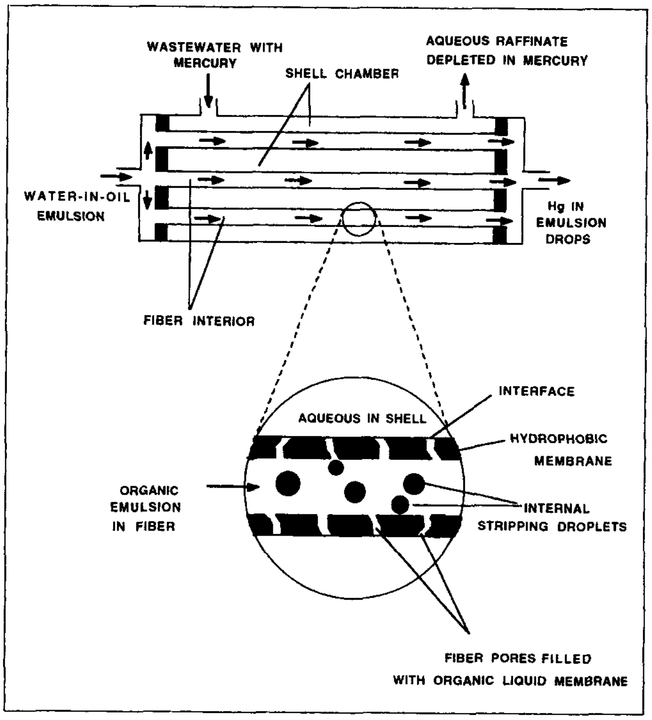
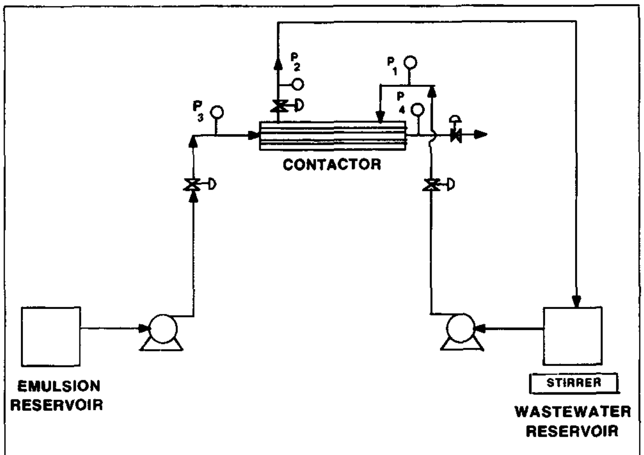


Figure 2. Extraction using a hollow-fiber contactor.

Interface is maintained at the pore mouth on the fiber outer surface by keeping the aqueous-feed-phase pressure higher than that of the emulsion phase. Mercury(II) from wastewater is extracted into the organic phase of the emulsion by complexing with the carrier (oleic acid). The internal droplets containing the stripping agent (sulfuric acid) strip the complex to trap mercury as mercury (II) sulfate.

Another advantage of emulsion extraction in a hollow-fiber contactor is that while the pores are of the order of 0.05 micron in diameter, the internal-phase drops are of the order of 1-10 micron in the emulsion. It is unlikely that the internal droplets of the emulsion will be present in the membrane pores. Thus, there is only pure diffusion of the metal organic complex within the pores, and stripping will occur only in the fiber lumen. Since the aqueous-phase resistance is expected to dominate, the exclusion of the droplets from the pores is not expected to change overall transfer rates. On the other hand, it could prove to be advantageous since this exclusion of the internal aqueous droplets would prevent direct contact with the outer water phase, thus minimizing leakage and swell observed in stirred contactors.

Other configurations for simultaneous extraction and stripping include supported liquid membrane (SLM) and hollow-fiber-contained liquid membrane (HFCLM). The SLM configuration has the organic-phase liquid (containing the metal complexing agent) immobilized in the pores of a microporous membrane with the aqueous feed phase flowing on one side and the aqueous strip phase on the other side. A major dis-



Manufacturer's Module Specifications

Fiber i.d./o.d.	240/300 microns	Module diameter	2.5 cm
Pore size	0.05 microns	Module length	20 cm
Porosity	30 %	Effective surface area	4000 cm^2
Effective fiber length	16 cm		
Number of fibers	3600		

Figure 3. Experimental setup for studying extractions.

advantage of SLMs is their instability due mainly to loss of extractant and/or organic solvent into the flowing aqueous phases because of solubility and short-circuiting of the two aqueous phases if pressure differential across the membrane exceeds capillary forces holding the organic liquid in the pores (Danesi et al., 1987). The HFCLM configuration has two sets of microporous hollow-fiber membranes, one carrying the feed phase and the other the strip phase (Majumdar et al., 1992; Sengupta et al., 1988). The organic liquid is contained between these two sets of fibers by maintaining the aqueous phases at a higher pressure than the organic phase but lower than its breakthrough value. HFCLM offers long-term stability since the membrane liquid is connected to a reservoir and is continuously replenished to make up for any loss by solubility. The major disadvantage here is the difficulty in mixing the two sets of fibers to achieve a low contained liquid membrane thickness. Present reported thicknesses are large and could yield low fluxes if diffusion through the membrane is limiting. ELM extraction in hollow-fiber contactors can offer long-term stability as the organic phase of the emulsion continuously replenishes the liquid in the pores. A literature search revealed only one previous reference (a patent) in this area (Anon, 1991).

Experimental Studies

Emulsion extractions of mercury, copper and nickel from aqueous streams were studied in a hollow-fiber contactor (Liqui-Cel Model 5 PCM-100, Hoechst Celanese, Charlotte, NC) details of which are given in Figure 3. These are hydrophobic hollow fibers made of polypropylene. These fibers are reported to show very good chemical stability and can be used over the entire pH range. The experiments were run in a semibatch manner at treat ratios (ratio of aqueous feed volume to emulsion volume) of 5 and 10 to allow for direct comparison with results of emulsion liquid membrane extractions in a batch stirred contactor.

Figure 3 shows the experimental setup. All experiments were run with a stationary emulsion in the fiber lumens and the aqueous waste stream flowing through the shell in total recycle mode. The pressure on the shell side was maintained at 5–10 psig (34–69 kPa), higher than the lumen pressure but lower than the breakthrough value. The metal extracting agents used in the membrane phase were LIX 84 (a hydroxy oxime supplied by Henkel Corporation) for copper, di-2-ethyl hexyl phosphoric acid for nickel, and oleic acid for mercury. The coarse emulsions were made by blending the ingredients (solvent tetradecane containing the metal extracting agent, a Paramins surfactant ECA 5025 supplied by Exxon, and the interal stripping phase, 6N sulfuric acid) in a high-speed Waring blender for 2 min. Typical emulsion formulation had 1–3 wt. % surfactant, 5–10 wt. % extracting agent and 15–25 wt. % of internal stripping phase in tetradecane. The exact formulations are listed in the figure captions for each experiment. The water contents for the fresh and spent emulsions were determined by Karl Fisher titrations. Heavy metal concentrations in the aqueous reservoir were measured at different times by flame atomic absorption spectroscopy. Initial metal concentration in aqueous feed phase was 1,000 ppm for all runs except for mercury which was 500 ppm. Leakage of internal-phase stripper, sulfuric acid, into the feed phase was measured by analyzing the sulfate concentration in the feed phase by ion chromatography.

Results and Discussion

Figure 4 compares extraction rates for copper removal using an emulsion liquid membrane in a hollow-fiber contactor and stirred contactor. While rates of extraction are higher in the

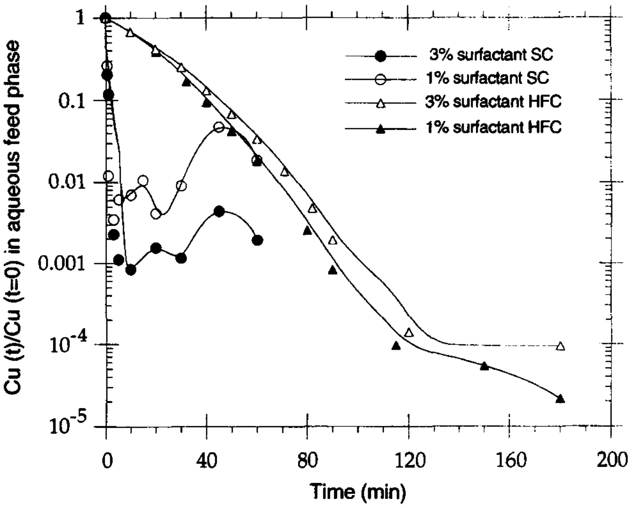


Figure 4. Effect of surfactant concentration in emulsion on copper extraction in a stirred contactor (SC) and hollow-fiber contactor (HFC).

Extracting agent in ELM = 5 wt. % LIX 84; Internal stripping phase wt. % in ELM = 18; Treat ratio = 10; pH of aqueous feed phase = 5.36.

SC: stirrer RPM = 400; volume of aqueous feed phase = 300 cm^3; volume of ELM = 30 cm^3.

HFC: aqueous flow rate in shell = 40 cm^3/min; volume of aqueous feed phase = 270 cm^3; volume of ELM = 27 cm^3.

Table 1. Comparing Swell and Leakage for ELM Extraction in Stirred Contactor (SC) and Hollow-Fiber Contactor (HFC)*

System	wt. % Water in ELM Initial/Final	% Swell	% Leakage
Copper Extraction			
HFC 3% surfactant; TR = 10	14.5/14.1	0	0.02
1% surfactant; TR = 10	14.1/13.6	0	0.00
SC 3% surfactant; TR = 10	16.6/32.3	95	7.90
1% surfactant; TR = 10	13.0/16.5	27	40.00
Nickel Extraction			
HFC 1% surfactant; TR = 5	14.7/14.7	0	0.30
Mercury Extraction			
HFC 3% surfactant; TR = 5	12.2/14.3	20	0.00

* Treat ratio (TR) is the ratio of feed-phase volume to emulsion volume.

stirred tank because of larger interfacial areas, fluxes are comparable and the hollow-fiber contactor is able to reduce copper levels an order of magnitude lower than the stirred tank. The leakage of the internal-phase contents into the feed phase is 0.02% for the hollow-fiber contactor, while it is as high as 8% for the stirred contactor which accounts for the improved extraction. The copper concentration never falls below 1 ppm in the SC extractions, while it goes down to as low as 20 ppb in the HFC. Further, the water in the emulsion phase swells from 16 wt. % to 33 wt. % in the stirred tank, while there is essentially no swell in the HFC (Table 1). Swelling dilutes metal as well as stripping reagent concentration in the internal phase. It also makes the emulsion more viscous and difficult to demulsify.

The advantage of using a hollow-fiber contactor becomes more apparent when using less stable emulsions. A less stable emulsion with low surfactant concentration would swell less and also be less difficult to demulsify after the extraction. However, it would also display higher leakage rates in the stirred tank as the emulsion ruptures more easily. The formulation of the emulsion is an optimization between ease of product recovery and leakage stability. Figure 4 compares extraction of copper in the two contactors when the emulsion is formulated with 1% surfactant. The stirred tank run fails, displaying leakages as high as 40% while the leakage in the hollow-fiber contactor is only 0.02% (Table 1). Thus, emulsion stability is not a factor in the HFC.

This result is important since a significant amount of research on emulsion liquid membrane extractions focuses on tailormaking a stable emulsion for each process. The surfactant that stabilizes an emulsion for one system may not work for another because of interactions with the extracting agent or the stripping agent. For some systems, the liquid membrane viscosity has to be increased to reduce leakage even though this could reduce diffusion rates through the membrane and make the downstream demulsification more difficult. The internal-phase volume fraction is also limited by stability considerations. These factors are irrelevant in a hollow-fiber contactor extraction. In fact, it is possible to extrapolate this observation all the way to zero surfactant concentration where the "emulsion" is an oil-strip-phase mixture free of surfactant. Figure 5 compares extraction of copper from an aqueous feed in a hollow-fiber contactor using an emulsion- and an oil-strip-phase mixture. The extraction utilized total recycle of both the aqueous and emulsion phases in a cocurrent mode. In this configuration, some stripping may be occurring in the emulsion feed reservoir. The extraction curves are similar for the emulsion and oil-strip mixture, indicating that the stripping is not rate-controlling for copper extraction. This observation was confirmed by once-through mode extractions with oil-strip mixtures. There is practically no leakage of the strip phase into the feed phase or the feed into the strip phase. The latter was

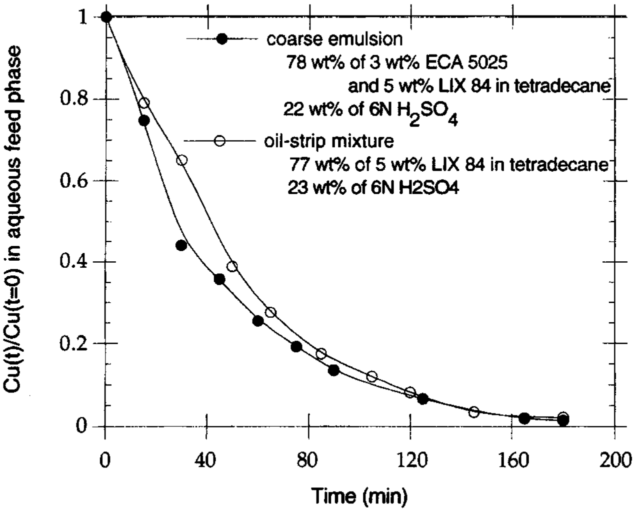


Figure 5. Comparing emulsion liquid membrane and oil-strip mixture extractions of copper in a HFC.

Shell: aqueous feed phase with pH = 1.6; flow rate = 62.8 cm^3/min; volume = 317.6 cm^3.
Tubes: emulsion or oil-strip mixture; flow rate = 117 cm^3/min; volume = 250 cm^3.
Configuration: total recycle of both phases.

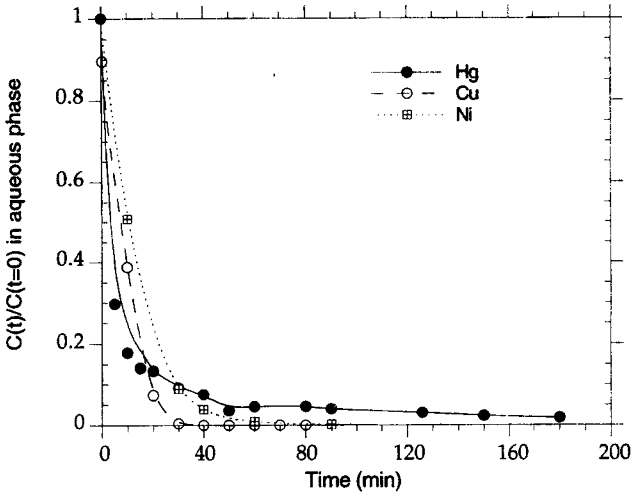


Figure 6. Comparing HFC extractions with ELM for Hg, Cu and Ni.

Extracting agent concentration in ELM = 10 wt. % for Hg and 5 wt. % for Cu and Ni; Surfactant concentration in ELM = 3 wt. % for Hg and Cu and 1 wt. % for Ni; Internal stripping phase wt. % in ELM = 15.2 for Hg, 18 for Cu and 20 for Ni; Treat ratio = 5; pH of aqueous feed phases are 2.7, 5.36, and 7.3 for Hg, Cu and Ni, respectively.
Shell: aqueous feed phase; flow rate = 40 cm^3/min; volume = 135 cm^3.
Tubes: stationary ELM; volume = 27 cm^3.

checked by analyzing for sodium ions in the strip phase to detect if there was leakage of sodium ions from the feed which contained a sodium acetate buffer.

Successful extractions of nickel and mercury have also been carried out in these extractors (Figure 6): 99% extraction of nickel and 96% extraction of mercury were achieved within 1 hour of operation. Stirred tank extractions of these metals result in swollen emulsions containing up to 45 wt. % water from an initial content of 11-15 wt. % water.

A more systematic investigation of the above process is underway. Important mass-transfer resistances for this process are aqueous-phase resistance, reaction at the interface of the emulsion and aqueous waste stream, diffusional resistance due to the hollow-fiber membrane pores, diffusion of the metal complex to the stripping phase of the emulsion and interfacial reaction at the interface between the membrane phase and stripping phase.

Experiments are also being performed to study extractions with oil-strip-phase mixtures with no surfactants in hollow-fiber contactors. These may also be looked upon as a supported liquid membrane with a continuous supply of membrane oil phase to replenish the membrane pores and ensure a stable long-term operation. This configuration has been suggested by others (Teramoto and Tanimoto, 1983), but never thoroughly investigated.

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