# Removal of Pollutants and Recovery of Toxic Heavy Metals from Wastewater Using Microporous Hollow Fiber Modules

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EXTENDED ABSTRACT

Multiphase equilibrium-based processes for separation and purification generally utilize dispersed systems in which one phase is dispersed in the other as bubbles or drops or thin films. Using microporous membranes, novel techniques have been developed such that multiphase processes can now be carried out in a nondispersive fashion for gas-liquid (Sirkar, 1992) and liquid-liquid (Prasad and Sirkar, 1992) contacting processes. Among such processes, only nondispersive solvent extraction of pollutants using microporous membranes will be of concern here. These processes employ immobilized immiscible phase interfaces at the pore mouths in a microporous membrane. Through such interfaces, solutes are extracted into the solvent as two immiscible phases flow on two sides of a microporous membrane. Many advantages of such a technique over conventional dispersion-based extractors have been summarized (Prasad and Sirkar, 1992).

Solvent extraction selectively extracts the solute/pollutant into the solvent from the feed aqueous solution. If it is desired to further have the pollutant selectively transferred into another aqueous phase in a concentrated form, a membrane may be employed between the two aqueous phases. Liquid membranes are particularly useful for such purification-concentration. Practical utilization of such techniques using, say, supported liquid membranes (SLMs) have encountered problems due to their inherent instability (Danesi et al., 1987).

The recently developed technique of the hollow fiber contained liquid membrane (HFCLM) is, unlike the supported liquid membrane, highly stable (Majumdar et al., 1992). Unlike membrane-based solvent extraction which requires only one immobilized phase interface in a microporous membrane, there are two immobilized phase interfaces in two different sets of microporous hollow fiber membranes in a module used in HFCLM technology. Feed aqueous solution containing the pollutant flows through the bores of one set of fibers while a strip aqueous solution flows through the bores of the other set of fibers. Any loss of the liquid membrane, contained between the two fiber sets on the shell side, is automatically replenished from an external membrane liquid reservoir. The pollutant is first selectively extracted into the liquid membrane from the feed fiber set, and then it is back extracted and concentrated into the strip aqueous solution flowing through the other

fiber set.

There are a wide variety of pollutants e.g. biological waste, organic pollutants and inorganic waste (both non-metallic and metallic). Many of the concepts mentioned earlier have potential applications in separations required for such pollutants in wastewaters.

This article is focussed of applications of these immobilized interface-based techniques to pollution control and/or recovery from industrial wastewaters as well as modeling the performances of microporous hollow fiber devices based on such techniques. The organic pollutants studied in this work are classified as priority pollutants; the inorganic compounds studied were toxic heavy metals. The membrane solvent extraction technique was used to remove priority organic pollutants as well as toxic heavy metals from the wastewater. The HFCLM technique was utilized to remove heavy metals from an aqueous stream and then simultaneously concentrate and recover the metal in a strip aqueous solution. The technique is generally not useful for priority organic pollutants; however the HFCLM technique has been successfully employed for the case of polar organic compounds like phenol and acetic acid which can be removed and concentrated through acid-base reaction in a HFCLM module (Sengupta et al., 1988; Basu and Sirkar, 1991).

The application and analysis of equilibrium-based membrane solvent extraction using a microporous hollow fiber (MHF) module is studied in the first phase of the work. Five Priority organic pollutants(phenol, 2-chlorophenol, nitrobenzene, acrylonitrile and toluene) have been simultaneously removed from a high strength synthetic wastewater to the level of around 5-25 $mg/\ell$; this technique was then applied to remove toluene from a real industrial wastewater which contained particulate matter. Lumped mass transfer analysis was done to predict the tube-side mass transfer behavior; the percent solute removal was also predicted by a semi-empirical method developed here.

In the second phase of the work, reversible chemical complexation-based solvent extraction using the same MHF module used for priority organic pollutants has been explored. Toxic heavy metals ($Cu^{2+}$ and $Cr^{6+}$) were individually removed in separate experiments form a synthetic wastewater by organic extractants. The organic extractant used for copper extraction was 5-20 v/v % LIX84 diluted in n-heptane and that for chromium extraction was 30 v/v % TOA diluted in xylene. For the prediction of copper extraction from the aqueous synthetic wastewater, a mathematical model was developed. The equilibrium constant and the forward interfacial chemical reaction rate constant were determined respectively by the linear regression of the experimental partitioning data and a trial-and-error method to obtain the best fit of the experimental solvent extraction data from a hollow fiber module.

In the third phase, the application of the HFCLM technique to the removal and simultaneous recovery of toxic metals like $Cu^{2+}$, $Cr^{6+}$, and $Hg^{2+}$ from synthetic wastewaters is considered. Toxic heavy metals can be transferred from the feed side aqueous phase to the strip side aqueous phase through the liquid membrane filled between two sets of fiber bundles by the countertransport mechanism for cations like

$Cu^{2+}$ and by the cotransport mechaanism for anions incorporating $Cr^{6+}$ and $Hg^{2+}$. The liquid membrane was 20 v/v % LIX84 diluted in n-heptane for $Cu^{2+}$ and 20 v/v % TOA diluted in xylene for $Cr^{6+}$ and $Hg^{2+}$; 5 v/v % 2-ethylhexyl alcohol was added to the liquid membrane as a modifier for $Cr^{6+}$. Five different HFCLM modules were used for these studies. Some of these modules were very highly packed, other were not; a few modules were long although most were short in length. Most modules had the same amount of membrane surface area on both sides, whereas a few had different areas on the two sides. The fibers in most modules were very well mixed but a few had fibers not very well mixed.

Even though the contained liquid membrane in a HFCLM module is instantaneously replenished from the membrane liquid reservoir, the liquid membrane composition will change with time for multicomponent liquid membranes. Therefore the long term behavior of a HFCLM module for the removal and the recovery of copper was tested experimentally and predicted theoretically via a mathematical model in the last phase. The results of the theoretical predictions are used to explore the proper position of the liquid membrane reservoir vis-a-vis the correct end of the HFCLM module to achieve a stable performance of the HFCLM module. For additional verification of the mathematical model suggested, the long term flux behavior of a HFCLM module during citric acid removal/concentration was predicted and compared with those published by earlier researchers (Basu and Sirkar, 1991).

LITERATURE CITED

Basu, R.; Sirkar, K.K. "Hollow Fiber Contained Liquid Membrane Separation of Citric Acid". *AIChE J.* **1991**, 37(3), 383.

Danesi, P.R.; Reichley-Yinger, L; Rickert, P.G. "Lifetime of Supported Liquid Membranes: the influence of interfacial properties, chemical composition and water transport on the long term stability of the membranes". *J. Membr. Sci.* **1987**, 31, 117.

Majumdar, S.; Sirkar, K.K.; Sengupta A. "Hollow Fiber Contained Liquid Membrane". in: *Membrane Handbook*, W.S. Winston Ho and K.K. Sirkar, eds., Van Nostrand Reinhold, New York, **1992**.

Prasad, R.; Sirkar, K.K. "Membrane-Based Solvent Extraction". in: *Membrane Handbook*, W.S. Winston Ho and K.K. Sirkar, eds., Van Nostrand Reinhold, New York, **1992**.

Sengupta, A.; Basu, R.; Sirkar, K.K. "Separation of Solutes from Aqueous Solutions by Contained Liquid Membranes". *AIChE J.* **1988**, 34, 1698.

Sirkar, K.K. "Other New Membrane Processes". in: *Membrane Handbook*, W.S. Winston Ho and K.K. Sirkar, eds., Van Nostrand Reinhold, New York, **1992**.