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To cite this Article Ilias, S. , Schimmel, K. A. and Yezek, P. M.(1999) 'NONDISPERSIVE LIQUID-LIQUID EXTRACTION OF COPPER AND ZINC FROM AN AQUEOUS SOLUTION BY DEHPA AND LIX 984 IN A HOLLOW FIBER MEMBRANE MODULE', Separation Science and Technology, 34: 6, 1007 — 1019
To link to this Article: DOI: 10.1080/01496399908951078
URL: http://dx.doi.org/10.1080/01496399908951078

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SEPARATION SCIENCE AND TECHNOLOGY, 34(6&7), pp. 1007–1019, 1999

NONDISPERSIVE LIQUID-LIQUID EXTRACTION OF COPPER AND ZINC FROM AN AQUEOUS SOLUTION BY DEHPA AND LIX 984 IN A HOLLOW FIBER MEMBRANE MODULE

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ABSTRACT

A liquid-liquid extraction procedure was used to study the amounts of Zn^{2+} and Cu^{2+} that could be simultaneously extracted from aqueous solution with di(2-ethylhexyl) phosphoric acid (DEHPA) and LIX 984 diluted with *n*-heptane at equilibrium. LIX 984 is a 1:1 volume blend of LIX 860 (5-dodoecylsalicylaldoxime) and LIX 84 (2-hydroxy-5-nonylacetophenone oxime). At equilibrium, a 0.3 mol/L DEHPA–20% (v/v) LIX 984 solution extracted 99% of both the zinc and copper from a solution that had 100 ppm of each metal.

A polysulfone hollow-fiber membrane module with 1 mm ID and 5,000-molecular weight cutoff was used to study the amounts of Zn^{2+} and Cu^{2+} that could be simultaneously extracted with a mixture of DEHPA and LIX 984. The aqueous and organic streams were operated at 100% recycle. With a 0.6 mol/L DEHPA–10% (v/v) LIX 984 solution, a 90.5 ± 1.7% (s.d.) extraction of zinc and a 93.70 ± 0.79% (s.d.) extraction of copper was obtained after 180 min.

INTRODUCTION

There is an increasing environmental concern for heavy-metal contamination of groundwater and soil from industrial wastewater discharge. In particular, the selective removal of Resource Conservation and Recovery Act (RCRA) contaminants such as Cd, Cu, Zn, Cr, Hg, and Zn from high-volume wastewater is a high-priority need in many governmental and industrial sites. Development of technologies for the selective removal

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of RCRA contaminants continues to be a major challenge. Current practices use precipitation or ion exchange and create waste solids that have to be disposed of in a landfill. Electrochemical metal recovery is a promising alternative: however, waste streams are often too dilute in metals and have low plating efficiencies (1). There is a growing need for the development of an effective and efficient method of removal and recovery of such metals from dilute solutions.

One way of recovering metals from wastewater, prior to discharge, would be to use liquid-liquid extraction. Liquid-liquid extraction uses a solvent, which is immiscible in water, to extract the metal from the wastewater. Extraction, however, still produces a waste solvent, contaminated with the metal, that has to be disposed of. There have been recent studies in which liquid membranes were used to remove and recover the metals. Liquid membranes may offer an attractive alternative to conventional solid or liquid ion-exchange processes where large volumes of solution require treatment (2). Membrane separation processes are often more capital and energy efficient when compared with conventional separation processes. Membrane devices and systems are almost always compact and modular (3).

Two types of membranes are Emulsion Liquid Membrane (ELM) and Supported Liquid Membrane (SLM). An ELM process includes four steps: (a) emulsification, (b) dispersion, (c) settling, and (d) breaking the emulsion. The advantage of using an ELM is that it combines the extraction and stripping in a single operation, which eliminates equilibrium limitations and reduces metal concentrations in the feed to very low levels (3). Two main disadvantages of a ELM are swelling and leakage of the emulsion. An SLM uses an organic liquid that is immobilized in the pores of a microporous membrane interposed between two aqueous solutions. One advantage of using an SLM is it can be selective for particular solutes. The major disadvantage of an SLM is its lack of long-term membrane stability as the solvent slowly dissolves into the aqueous phase unless it is 100% immiscible (3).

An alternative to ELMs and SLMs is a Hollow-Fiber Contained Liquid Membrane (HFCLM). An HFCLM consists of microporous hollow fibers arranged in a shell-and-tube configuration. HFCLM permeation-separation may be applicable to almost any separation problem to which other liquid membrane techniques have been applied (3). The HFCLM can offer a very high surface area to volume ratio without dispersion or mixing of the two phases (4).

To help enhance extraction rates, a chemical reaction is often employed in an extraction process (2). One of the most widely studied extracting agents for zinc is DEHPA (5). It extracts Zn(II) more effectively than other bivalent transition metals (6). It is a pH-dependent extractant, is chemically stable, and has good loading and stripping characteristics; its low aqueous solubility makes it one of the most versatile extractants available (7). For extraction of copper, the LIX line of agents have been widely investigated (8). Because of its low solubility in water, LIX 984 is widely used for extraction of copper from aqueous solution. LIX 984 is a 1:1 volume blend of two oximes, LIX 860 (5-dodoecylsalicylaldoxime) and LIX 84 (2-hydroxy-5-nonylacetophenone oxime). In this work, we investigated the simultaneous extraction of zinc and copper from dilute aqueous solution by nondispersive liquid-liquid extraction using extracting agents DEHPA and LIX 984 in a hollow-fiber membrane module.

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EXPERIMENTAL MATERIALS/METHODS

Materials and Sample Preparation

The source for Zn^{2+} was $ZnSO_4 \cdot 7H_2O$ and for Cu^{2+} it was $CuSO_4 \cdot 5H_2O$ (both from Fisher Scientific). The diluent was technical-grade *n*-heptane (Fisher Scientific). The DEHPA was provided by Albright and Wilson America, and LIX 984 was obtained from the Henkel Corporation.

The hollow-fiber membrane module used was a polysulfone Xampler UFP-5-E-3A module (A/G Technology Corporation). The characteristics of the membrane modules are as follows:

Nominal molecular weight cutoff (NMWC):	5000
Fiber internal diameter:	1 mm
Module length:	33.7 cm
Module diameter:	0.9 cm
Membrane area (based on inside diameter):	0.007 m^2
Nominal number of fibers:	12
Lumen nominal holdup volume:	3 mL
Shell nominal holdup volume:	5 mL
Porosity:	80%
Wall thickness (including skin):	0.3 mm

The tubing used in the experimental setup was Norton Pharmed NSF-51 tubing (Fisher Scientific), which is chemically resistant to the organic phase. The pH was measured using a Fisher Accumet 925 pH/ion meter. The concentrations of zinc and copper in the aqueous

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solutions were determined using a GBC 932 atomic absorption (AA) spectrophotometer at 213.9 nm and 324.7 nm, respectively.

The aqueous Zn^{2+} solution was prepared by dissolving 0.4398 g of $ZnSO_4{\cdot}7H_2O$ in distilled water, and the solution was made up to 1000 mL in a volumetric flask. The aqueous Cu^{2+} solution was prepared by dissolving 0.3929 g of $CuSO_4{\cdot}5H_2O$ in distilled water, and the solution was made up to 1000 ml in a volumetric flask. The aqueous Zn^{2+}-Cu^{2+} solution was prepared by dissolving 0.4398 g of $ZnSO_4{\cdot}7H_2O$ and 0.3929 g of $CuSO_4{\cdot}5H_2O$ in distilled water, and it was diluted to 1000 mL in a volumetric flask. The initial pH levels of the zinc and copper solutions were adjusted using a 1% (v/v) sulfuric acid solution or a 0.1 *M* sodium acetate solution.

The 0.3-mol/L DEHPA solution was prepared by pipetting 99.3 mL of DEHPA into a 1000-mL volumetric flask containing *n*-heptane. The 20% (v/v) LIX 984 solution was prepared by pipetting 200 mL of LIX 984 into a 1000-mL volumetric flask that contained *n*-heptane. The 0.3-mol/L–20% (v/v) LIX 984 solution was prepared by, first, pipetting 99.3 mL of DEHPA and, then, 200 mL of LIX 984 into a 1000-mL volumetric flask that contained *n*-heptane. The 0.6-mol/L DEHPA–10% (v/v) LIX 984 was prepared by pipetting 198.6 mL of DEHPA and, then, 100 mL of LIX 984 into a 1000-mL volumetric flask that contained *n*-heptane. Next, the solutions were made up to 1000 mL with *n*-heptane. A Teflon stir bar was placed in the flasks, and the solutions were stirred for 10 min using a magnetic stir plate to allow for complete mixing.

Methods

The purpose of this study was to obtain greater than 90% extraction of both zinc and copper. The work was divided into two parts: liquid-liquid extraction (LLE) and hollow-fiber membrane experiments. In part one, a system that extracts both zinc and copper was investigated at equilibrium. In part two, a polysulfone hollow-fiber membrane module was used to extract zinc and copper from an aqueous to an organic solution.

For the LLE experiments, 50 mL of each solution (phase ratio of 1:1 aqueous and organic) was pipetted into a 125-mL separatory funnel. Next, the samples were agitated for 30 min at a shaker motion of 100 cycles per minute. An experiment was performed to determine the shaking time needed to reach equilibrium, and it was determined to be 30 min. The samples were then allowed to settle so that the phases would separate. The aqueous phase was drawn off, and the equilibrium pH was measured and recorded. The aqueous samples were analyzed for zinc and copper content using AA spectrophotometer. The LLE data are reported as an average of four replicates.

The experimental setup of the hollow-fiber nondispersive LLE process is shown in Figure 1. For the hollow-fiber membrane experiments, the aqueous reservoir was operated at atmospheric pressure. The organic reservoir was connected to a pressurized air line. If the organic-phase pressure is higher than the aqueous phase, an immobilized aqueous/organic interface will exist on the outside surface of each hollow fiber. The aqueous/organic interface will be immobilized at the pore mouths on the aqueous side (tube side) of the membrane. The aqueous phase will not be dispersed in the organic phase and vice versa. At this interface, the solute from the aqueous phase will be partitioned into the organic phase. Therefore, compressed air was used to maintain a stable organic-aqueous interface.

A number of experiments were performed using a wide range of flow rates of the organic and aqueous phases and transmembrane pressure differences to determine desired operating conditions for the LLE. Based on these experiments, the desired flow rates for this hollow-fiber system were found to be 78 mL/min for the tube side (aqueous phase) and 77 mL/min for the shell side (organic phase). The shell-side pressure was maintained at 1.25 psig. Each reservoir volume was 300 mL. The extraction was allowed to continue for 120 min with 100 % recycle of both phases. Samples were taken at 5, 10, 15, 30, 45, 60, and 120 min to follow the extraction. The amount of sample and the final pH were measured and recorded. Then the samples were analyzed for zinc and copper content by AA spectrophotometer.

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RESULTS AND DISCUSSION

Two types of experiments were performed to investigate the effectiveness of DEHPA and LIX 984 as extractants for the extraction of copper and zinc metal ions from aqueous solution. Liquid-liquid extraction was used to determine at equilibrium how much zinc and copper could be extracted with DEHPA and LIX 984. The hollow-fiber membrane module was used to determine the nonequilibrium behavior of nondispersive LLE.

LLE Experiments

In LLE experiments, the effectiveness of 0.3 mol/L DEHPA and 20% (v/v) LIX 984 extracting agents for the simultaneous extraction of zinc and copper metal ions from

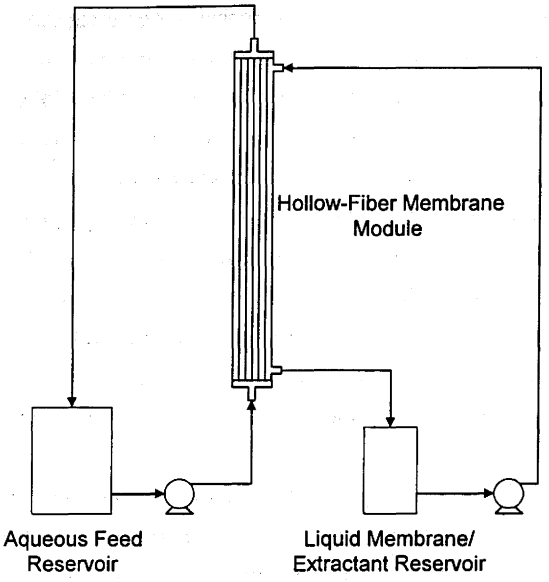

FIGURE 1. Schematic of hollow-fiber membrane LLE experimental setup with 100% recycle.

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aqueous solutions was investigated. The results are summarized in Table 1 for the simultaneous extraction of zinc and copper with (a) 0.3 mol/L DEHPA , (b) 20% (v/v) LIX 984, and (c) 0.3 mol/L DEHPA-20% (v/v) LIX 984 solutions. The LLE data are reported as an average of four replicates.

The results of the simultaneous extraction of zinc and copper with 0.3 mol/L DEHPA show that with an initial pH in the range of 3.0–4.1, 97% extraction of zinc and 43% extraction of copper can be obtained. From these results, it can be concluded that DEHPA preferentially extracts zinc over copper from aqueous solution. With 20% (v/v) LIX 984, the results of the simultaneous extraction of zinc and copper indicate that with an initial pH in the range of 3.1–5.0, 98% extraction of copper and only 0.6% extraction of zinc can be obtained. The results show that the LIX 984 has a higher affinity for the copper than for the zinc. Thus, it can be concluded that DEHPA prefers zinc and LIX 984 prefers copper.

The results of the simultaneously extraction of zinc and copper with a 0.3-mol/L DEHPA-20% (v/v) LIX 984 solution are given in Table 1. With an initial pH of 3.1, 99%

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TABLE 1. SIMULTANEOUS LIQUID-LIQUID EXTRACTION OF ZINC AND COPPER

	0.3 mol/L DEHPA		20% (v/v) LIX 984		0.3 mol/L DEHPA-20% (v/v) LIX 984	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
Initial pH	3.008	4.008	3.133	4.950	3.133	4.950
Equilibrium pH	2.072	2.103	2.451	2.692	2.577	2.095
Initial zinc conc. (mg/L)	75.00 ± 0.93	74.00 ± 3.00	103.577 ± 0.21	104.60 ± 0.140	103.57 ± 0.21	104.60 ± 0.14
Final zinc conc. (mg/L)	2.09 ± 0.45	1.43 ± 0.04	97.22 ± 0.51	103.60 ± 4.20	0.694 ± 0.04	5.42 ± 0.10
% zinc extracted	97.21 ± 0.60	98.06 ± 0.05	6.14 ± 0.50	0.90 ± 0.04	99.33 ± 0.04	94.82 ± 0.10
Initial copper conc. (mg/L)	93.05 ± 0.26	99.11 ± 0.43	90.05 ± 0.51	97.55 ± 0.41	90.05 ± 0.51	97.55 ± 0.41
Final copper conc. (mg/L)	52.36 ± 0.97	54.60 ± 1.80	0.66 ± 0.85	1.70 ± 1.10	0.071 ± 0.02	0.11 ± 0.06
% copper extracted	43.73 ± 0.52	44.91 ± 0.21	99.27 ± 0.61	98.26 ± 0.46	99.92 ± 0.41	99.88 ± 0.63

extraction of both zinc and copper can be obtained. The amount of zinc is slightly higher than the 98% extraction obtained with just the 0.3 mol/L DEHPA. This is due to the synergistic effect of the combination of DEHPA and LIX 984. A possible explanation for this effect is that zinc is extracted primarily by DEHPA and a small amount is extracted by LIX 984; therefore, once most of the zinc has been extracted by DEHPA, some of the remainder is also extracted by the LIX 984.

It should also be noted that since 99% extraction of zinc and copper was obtained by the 0.3 mol/L DEHPA–20% (v/v) LIX 984 solution, this solution cannot be used for selective extraction of copper from a zinc-copper system. However, for simultaneous extraction of copper and zinc from aqueous solution, it could be an excellent candidate for nondispersive LLE in a hollow-fiber membrane module.

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Hollow-Fiber Membrane Experiments

A number of experiments were performed in a hollow-fiber membrane module to determine the extent of extraction that can be obtained for zinc and copper using DEHPA and LIX 984 solutions, respectively. A wide range of flow rates was evaluated for the organic and aqueous phases in the shell and tube sides, respectively. The LLE experiments were performed in a closed loop. The concentration-versus-time data for extraction of zinc from aqueous solution in a hollow-fiber membrane module with 0.3 mol/L DEHPA solution are shown in Figure 2. The results are shown for three replicate runs at the indicated shell-side and tube-side flow rates. The mean percent extraction was 97.13 ± 0.97 (s.d.). This result is in agreement with results obtained in the LLE experiments. The concentration-versus-time profiles of three replicate runs for extraction of copper with LIX 984 in a hollow-fiber module are shown in Figure 3. From an inspection of Figures 2 and 3, it can be seen that zinc is extracted more rapidly with DEHPA than copper is extracted with LIX 984. However, it can be seen that if the experiment with copper was run longer (Figure 3), the amount of copper extracted would reach an asymptotic value around the 99% extraction that was achieved in the LLE experiments.

For the simultaneous extraction of zinc and copper, three replicate runs were performed using the 0.3 mol/L DEHPA–20% (v/v) LIX 984 solution. The results are summarized in Table 2. The experiments were performed in closed loops with total recycle for organic and aqueous streams. The shell side contained the organic phase, and the aqueous phase was circulated through the fiber lumens (tube side).

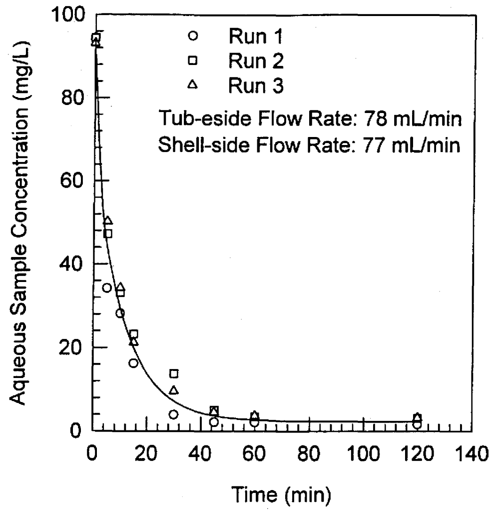

FIGURE 2. Extraction of zinc from aqueous solution in hollow-fiber membrane with 0.3 mol/L DEHPA solution.

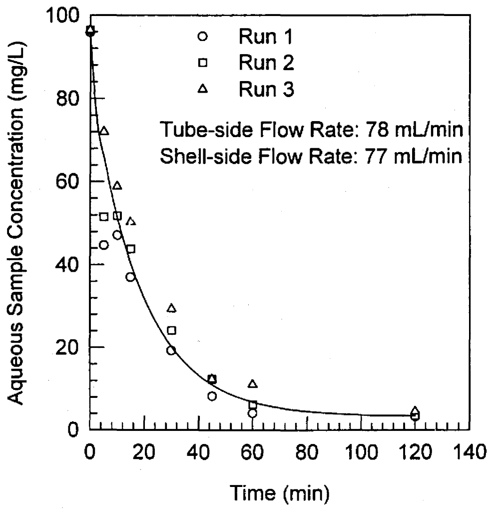

FIGURE 3. Extraction of zinc from aqueous solution in hollow-fiber membrane with 20% (v/v) LIX 984 solution.

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TABLE 2. SIMULTANEOUS HOLLOW-FIBER MEMBRANE MODULE EXTRACTION OF ZINC AND COPPER

	0.3 mol/L DEHPA–20% (v/v) LIX 984			0.6 mol/L DEHPA–10% (v/v) LIX 984		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
Initial pH	4.040	4.040	4.040	4.040	4.040	4.040
Final pH	2.427	2.398	2.428	2.427	2.398	2.428
Initial zinc conc. (mg/L)	94.51	94.51	94.51	96.24	96.24	96.24
Final zinc conc. (mg/L)	39.64	37.63	35.60	10.92	8.42	7.96
% zinc extracted	58.05	60.18	62.33	88.65	91.25	91.73
Initial copper conc. (mg/L)	99.73	99.73	99.73	95.58	95.58	95.58
Final copper conc. (mg/L)	7.47	6.305	6.24	6.67	6.19	5.19
% copper extracted	92.51	93.68	93.74	93.03	93.52	94.57

The concentration profiles of zinc and copper metal ions in the aqueous phase with time are shown in Figure 4. Over a period of 120 min, the mean percent extractions for zinc and copper were found to be 60.2 ± 2.1%, and 93.3 ± 1.7%, respectively. The percent extraction of zinc was considerably lower than that obtained from the LLE experiments, while that for copper was only slightly different. It is not clear what caused the lower extraction of zinc. One explanation is that the LIX 984 has a higher affinity (wetting tendency) for the membrane than does DEHPA.

To determine the effect of organic-phase composition on the extraction of copper and zinc, the concentration of DEHPA was doubled (from 0.3 mol/L to 0.6 mol/L) and the LIX 984 concentration was reduced by half (from 20% (v/v) to 10% (v/v)). The extraction experiments in the hollow-fiber membrane module were performed under similar hydrodynamic conditions. The results are tabulated in Table 2. The variation of zinc and copper metal ions in the aqueous phase with time is shown in Figure 5. In about 180 min, the copper and zinc metal-ion concentrations approach steady-state values. Over this period of time, the mean percent extraction for zinc was 90.5 ± 1.7% while that for copper was 93.7 ± 0.8%.

The results meet the goal of achieving greater than 90% extraction of both metals; however, this percentage is less than that achieved with the LLE experiments and with zinc and copper by themselves. Since the amount of metal that was extracted did increase when the time was increased, a higher extraction could be achieved if the experiment was run for a longer time. Other alternatives are to use more than one module or to try other concentrations of DEHPA and LIX 984 in the organic phase. However, it appears that the presence of a high mass transfer resistance in the immobilized organic phase (membrane pores filled with organic phase) could be responsible for the slow extraction of metal ions in closed loops. On the other hand, since the method is inherently based on nondispersive extraction, no phase separation is required for extraction. Thus, the proposed scheme may be found attractive as a stand-alone operation for extracting metal ions from contaminated aqueous streams.

CONCLUSIONS

A combination of DEHPA and LIX 984 can be used to simultaneously extract zinc and copper from an aqueous solution in liquid-liquid extraction, with over 99% extraction of both metal ions. For nondispersive liquid-liquid extraction in a hollow-fiber membrane

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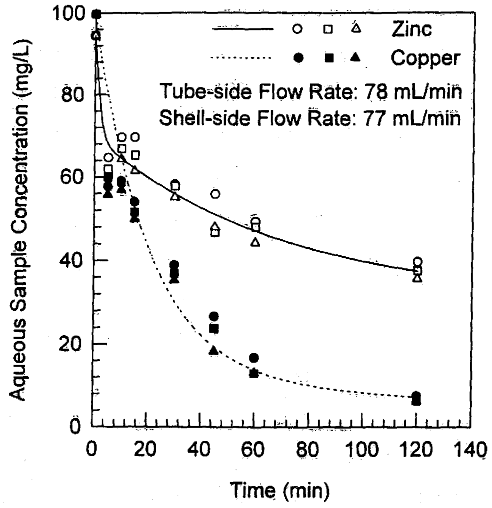

FIGURE 4. Simultaneous extraction of copper and zinc from aqueous solution in hollow-fiber membrane with 0.3 mol/L DEHPA-20% (v/v) LIX 984 solution.

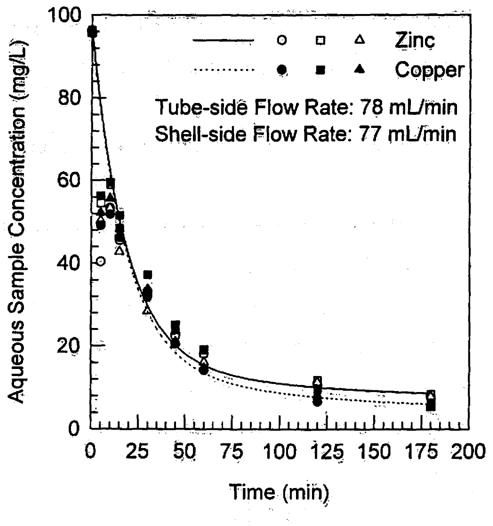

FIGURE 5. Simultaneous extraction of copper and zinc from aqueous solution in hollow-fiber membrane with 0.6 mol/L DEHPA-10% (v/v) LIX 984 solution.

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module with DEHPA and LIX 984, it is possible to extract more than 90% of the copper and zinc from the aqueous solution. Thus, the hollow-fiber membrane module provides an alternative to conventional LLE for the extraction of metal ions from aqueous solution.

ACKNOWLEDGMENTS

The authors would like to acknowledge the funding from the USEPA, Office of Exploratory Research, Washington, D.C., Grant No. R 8218304-01-0.

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