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S. Ilias[a]; K. A. Schimmel[a]; T. Nukunya[a]
[a] Department of Chemical Engineering, North Carolina A&T State University, Greensboro, North Carolina, U.S.A.

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STRIPPING OF Zn(II), Cu(II), Co(II), AND Cd(II) FROM DEHPA USING EDTA IN A HOLLOW-FIBER MEMBRANE MODULE

S. Ilias,* K. A. Schimmel, and T. Nukunya

Department of Chemical Engineering, North Carolina A&T
State University, Greensboro, North Carolina 27411

ABSTRACT

The equilibrium behavior of liquid-liquid extraction of Zn(II), Cu(II), Co(II), and Cd(II) from DEHPA (di(2-ethylhexyl)phosphoric acid) with EDTA (ethylenediamine-tetraacetic acid) was studied. A concentration of 0.003M EDTA was able to extract simultaneously 83, 70, 88 and 54% of the cadmium, cobalt, copper and zinc, respectively at a pH between 1.6 and 1.8.

The non-equilibrium liquid-liquid extraction behavior was studied using a polysulfonic hollow fiber membrane module with 1 mm ID and 5,000 molecular weight cut-off. The aqueous feed solution and EDTA was passed through the tubeside of the two membrane modules, and the organic DEHPA solution was circulated through the shellside. The optimum flow rate for the organic solution was 77ml/min and that of the aqueous feed and strip solutions were 78ml/min. The shellside pressure was maintained at 1.0-1.2 psig and that of the tubeside was kept at atmospheric pressure so that a stable organic interface was achieved. Under these conditions, 77, 63, 93, and 56% of cadmium, cobalt, copper and zinc were extracted from DEHPA, respectively.

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*Corresponding author.

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INTRODUCTION

The recovery of metals from dilute solutions is a frequent requirement in hydrometallurgical processing as well as for treating effluents from metallurgical and metal-finishing activities and other industries [1]. Metals like zinc, copper, cadmium and cobalt are found commonly in industrial wastewater. There is an increasing environmental concern of heavy metal contamination of groundwater and soil from industrial wastewater discharge.

Therefore, an effective and efficient way of removal and recovery of these metals from dilute solutions is necessary. Current practices use precipitation or ion exchange and create a sludge that has 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 [2].

One way of recovering metals from wastewater, prior to discharge, would be to use Liquid-Liquid Extraction (LLE). LLE 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.

There have been recent studies on using liquid membranes to remove and recover the metals. Liquid membranes may offer an attractive alternative to conventional solid or liquid ion exchange processes when large volume of solution require treatment [1]. 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 [3,4].

There are three types of Liquid Membranes (LM): Emulsion Liquid Membrane (ELM), Supported Liquid Membrane (SLM) and Hollow Fiber Contained Liquid Membrane (HFCLM). An ELM process has four steps: (1) emulsification, (2) dispersion, (3) settling, and (4) breaking the emulsion. The main advantages are that extraction and stripping take place in one single step, which eliminates equilibrium limitations inherent in LLE [3]. The main disadvantage of ELM is that the emulsion can swell and leak after prolonged contact with the feed phase [5]. The SLM uses an organic extractant immobilized in the pores of the membrane to extract the solute. The main advantage of this is that it can be very selective for particular solutes. The main disadvantage is that it is unstable due to loss of extractants into the flowing aqueous phase [6].

HFCLMs are able to overcome the shortcomings of ELMs and SLMs and still retain their advantages. They contain microporous hollow fibers that are arranged in a shell and tube configuration [7]. They offer a very high area/volume ratio without dispersion of the two phases and can operate in a variety of mode [8].

A chemical reaction is often employed to enhance extraction rates in an extraction process [3]. DEHPA is the most widely studied extracting agents for the extraction of divalent transition metals [9]. It is pH dependent, chemically stable and has good loading and stripping characteristics [10]. EDTA is one of the most widely used stripping agents. Its reactions are also influenced by pH and this plays a major role in complex formation [11]. Recently, we investigated simultaneous extraction of Zn(II) and Cu(II) from dilute aqueous solution using DEHPA in n-heptane as extracting agent (organic phase) via non-dispersive LLE in a hollow fiber membrane module [12]. The results showed that over 90% of Cu(II) and Zn(II) can be extracted from aqueous solution to DEHPA solution. To develop a non-dispersive liquid-liquid extraction and stripping (back-extraction) process, we investigated the simultaneous extraction of Zn(II), Cu(II), Co(II) and Cd(II) from aqueous solution to DEHPA in n-heptane and then back-extract the metal ions from DEHPA solution to the receiving aqueous EDTA solution in a two-membrane module configuration. The objective of this paper is to report equilibrium and non-equilibrium results on simultaneous back-extraction of these metal ions from DEHPA to EDTA solution.

EXPERIMENTAL MATERIALS/METHODS

Materials and Sample Information

Aqueous solutions of Zn(II), Cu(II), Co(II), and Cd(II) were prepared from $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$, $CoSO_4.7H_2O$ and $3CdSO_4.8H_2O$, respectively (all from Fisher Scientific). The source of EDTA used was Disodium Ethylenediamine Tetraacetic Acid (Fisher Scientific). DEHPA was obtained from Albright and Wilson America [9], and n-heptane was obtained from Fisher Scientific.

Two polysulfone membrane modules, Xampler UFP-5-E-3A (one for the extraction process and the other for the stripping reaction) from A/G Technology were used for the hollow fiber membrane experiments. The tubing used in the experimental setup was Norton Pharmed NFS-51 (Fisher Scientific). Four flow meters were used to measure the flow rates of the organic and aqueous solutions. The tube-side and shell-side pressures were measured by pressure gauges. A Fisher Accumet 925 pH/ion meter was used in measuring the pH of the aqueous solutions. A GBC 932 Atomic Absorption Spectrometer was used to determine the concentrations of the metal ions in the aqueous solutions.

A stock solution of 1000 ppm of Zn ions was prepared by 4.4g of $ZnSO_4.7H_20$ in distilled water to a volume of 1000 mL in a volumetric flask. Stock solutions of 1000ppm of each of Co, Cd, and Cu ions were also prepared in a similar way by dissolving 4.75, 4.44 and 3.85g of $CoSO_4.7H_2O$, $3CdSO_4.H_2O$ and $CuSO_4.5H_2O$, respectively in 1000ml volumetric flasks. A combination of zinc, cobalt, copper and cadmium metal ions of 1000 ppm each was prepared by dissolving 4.40, 4.75, 4.44 and 3.85g of $ZnSO_4.7H_2O$, $CoSO_4.7H_2O$, $CuSO_4.5H_2O$ and $3CdSO_4.8H_2O$, respectively into a 1000ml volumetric flask.

The pH of the solution was adjusted by adding drops of 1% (v/v) H_2SO_4 (to reduce pH) and 5N NaOH (to increase pH).

The stripping solution (0.1M EDTA) was prepared by dissolving 38.1g of disodium EDTA in distilled water in a 1000ml volumetric flask. A 1% (v/v) H_2SO_4 was prepared by diluting 1 mL of concentrated sulfuric acid in distilled water to a volume of 1000 mL in a volumetric flask. The 0.3 M DEHPA solution was prepared by pipetting 99.3 mL of DEHPA into a 1000 mL volumetric flask containing n-heptane and adjusted the final volume to 1000 mL mark.

Methods

The objective of this study was to extract cadmium, cobalt, copper and zinc from DEHPA using EDTA and to investigate any interference effects. The work was divided into two parts: liquid-liquid extraction (LLE) and non-dispersive LLE in hollow fiber membrane modules. In the equilibrium LLE equilibrium experiments, we investigated a system that extracts cadmium, cobalt, copper and zinc simultaneously. For non-dispersive LLE experiments, a polysulfone hollow fiber membrane module was used to back-extract cadmium, cobalt, copper and zinc from DEHPA to EDTA.

In the equilibrium LLE experiments, attention was focused on the back-extraction of Cd, Co, Cu and Zn from DEHPA into EDTA. For equilibrium extraction of metal ions from aqueous to organic DEHPA-phase, 50 mL each of the organic and aqueous solutions were measured into a 250 mL beaker. The two phases were mixed for about an hour using a magnetic stirrer. After the reaction, the mixture was allowed to separate into two phases. The organic phase was decanted into a 100ml beaker, and the pH of the aqueous phase was recorded. A 50 mL portion of the organic solution was measured into a clean 125ml polyethylene sample bottle, and was mixed with 50ml of the stripping solution (EDTA). The pH of the stripping solution was fixed by an appropriate buffer solution. The content of the bottle was shaken for 1 hour. The resulting mixture was then poured into a 125ml separating funnel and left for 20 minutes to separate into two phases before the aqueous phase was drained into a 50ml beaker. The pH of this solution was measured by the pH-meter, and a GBC Atomic Absorption Spectrometer measured the concentration of the stripped metal ions. The % of metal ions stripped was then calculated.

Figure 1 shows the experimental set-up of the hollow fiber non-dispersive liquid-liquid extraction process. Both the aqueous feed and the strip solutions were operated at atmospheric pressure. The organic reservoir was connected to a pressurized air-line. This is to ensure the organic phase pressure is higher than the aqueous phase pressure so that an immobilized aqueous/organic interface will exist in the pores of each of the hollow fibers. The reservoir volume used was 500

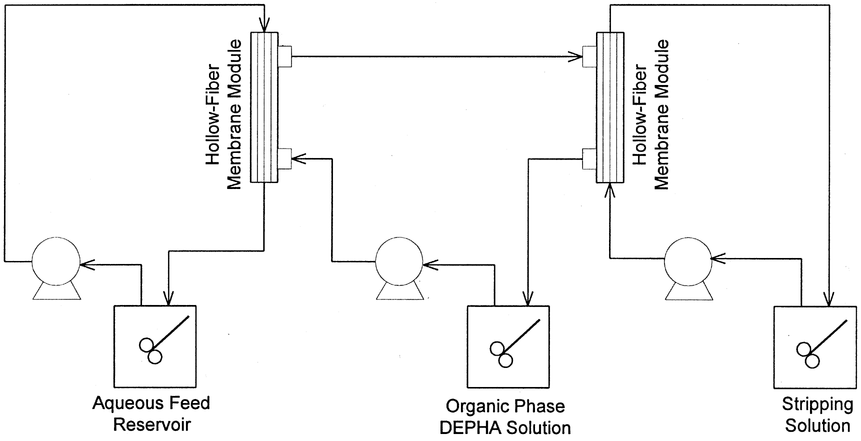

Figure 1. A schematic of a Hollow Fiber Membrane Set Up with 100% recycle.

ml. A series of experiments were performed using a wide range of the organic and aqueous phases and the transmembrane pressures to determine the desired operating condition. Based on these experiments, the desired stream flow rates for this hollow-fiber system were found to be 77 ml/min for the shellside (organic phase), 78 ml/min for tubeside aqueous feed, and 77 ml/min for the tubeside (stripping solution). The shellside pressure was maintained at 1.25 psig. The two-membrane module simultaneous liquid-liquid extraction and back-extraction (LLE & LLBE) experiment was conducted in batch mode with 100% recycle of the aqueous feed solution, organic phase DEHPA solution and stripping EDTA solution.

RESULTS AND DISCUSSION

Two main experiments were performed to investigate the effectiveness of EDTA in back-extracting Cd, Co, Cu and Zn simultaneously from DEHPA [13]. The first part involved using liquid-liquid extraction to determine at equilibrium how much of these could be extracted from DEHPA using EDTA. The second part involves the use of a hollow fiber membrane module in the non-dispersive LLBE of metal ions from organic DEPHA phase to aqueous EDTA phase.

Equilibrium LLBE of Metal Ions When Stripped Singly

These experiments were conducted to see the effect of pH on the % metal ions stripped without interference from other metal ions. The metal ions stripped are cadmium, cobalt, copper and zinc. Since pH is the driving force, the value of the concentration of the metal ions will depend on the pH of the solution at any time. It can be seen that a high degree of stripping of the metal ions is achieved at low pH values. This is because the efficiency of complex formation with EDTA is affected by a variation in pH of the solution, and this occurs at low pH values, which is known as the low pH effect [11]. It can be seen from Figure 2 that the percent copper stripped is the highest and the percent zinc is the lowest at low pH values. When compared to the plot of copper with that obtained by Kim [14], it can be seen that the shape is the same for both plots for copper. At low pH values, a high percentage of copper is extracted. This can be attributed to the combination of LIX 984 to the EDTA extractant.

Equilibrium LLBE Metal Ions When Stripped Simultaneously

In the LLBE experiments, the effectiveness of 0.003M EDTA in back-extracting Cd, Co, Cu and Zn from DEHPA was investigated. The extraction data are reported here as averages of two replicates. It can be seen from Figure 3

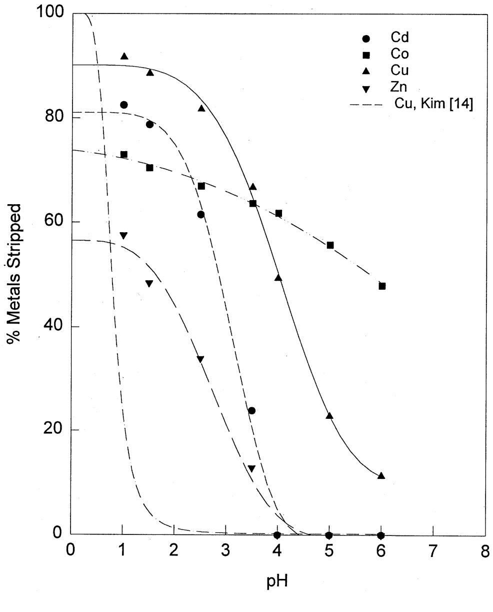

Figure 2. Effect of pH on stripping of 25 ppm each of cadmium, cobalt, copper and zinc in 0.3M DEHPA singly with 0.003 M EDTA using LLBE.

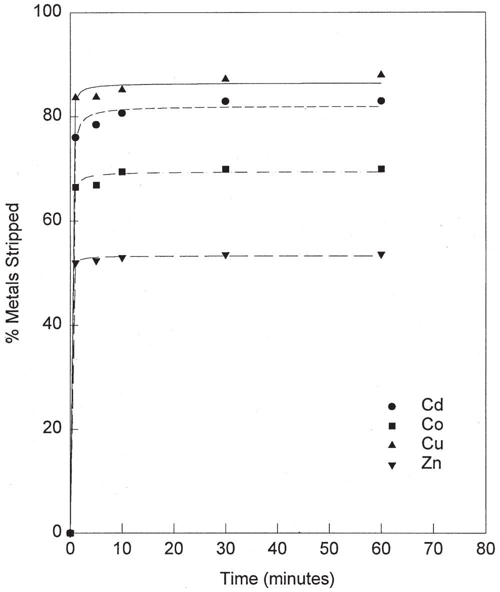

Figure 3. Stripping of 25 ppm each of cadmium, cobalt, copper and zinc, in 0.3M DEHPA simultaneously with 0.003M EDTA solution using LLBE.

that equilibrium is established in about 20 minutes. The percent Cu stripped (87.94%) is the highest and that for Zn (53.61%) is the lowest. This shows that the affinity of EDTA for the metal ions is in the order, Cu > Cd > Co > Zn.

LLBE Hollow Fiber Experiments

These experiments were run to determine if the hollow fiber membrane system could strip Cd, Co, Cu and Zn simultaneously. As measured by AAS, initial concentrations of metal ions were 25.02, 25.10, 25.01, and 25.07 ppm of Cd, Co, Cu and Zn, respectively. The DEHPA and EDTA concentrations were 0.3 M and 0.003 M, respectively. The initial pH of the aqueous feed solution containing the metal ions was 4.55 and that of the EDTA was 1.61. Figure 4 shows a graph of the percent metal ions stripped versus time. The results of this experiment are summarized in Table 1, Run #1. It can be seen that the hollow fiber membrane was able to strip more than 50% of the metal ions.

Other experiments were conducted to test if the interference of the metal ions on each other affected the percent of stripping. To test this, the concentra-

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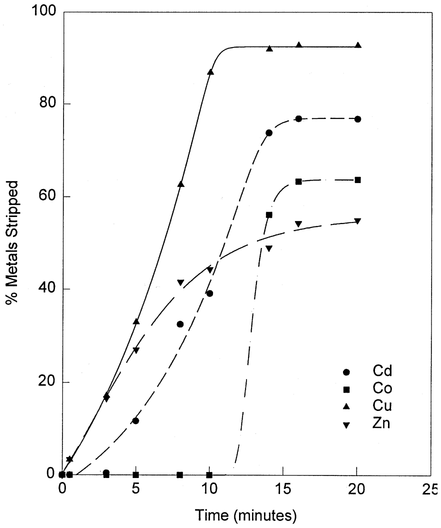

Figure 4. Stripping of 100 ppm each of cadmium, cobalt, copper and zinc, in 0.3M DEHPA simultaneously with 0.003M EDTA solution using hollow fiber membrane module.

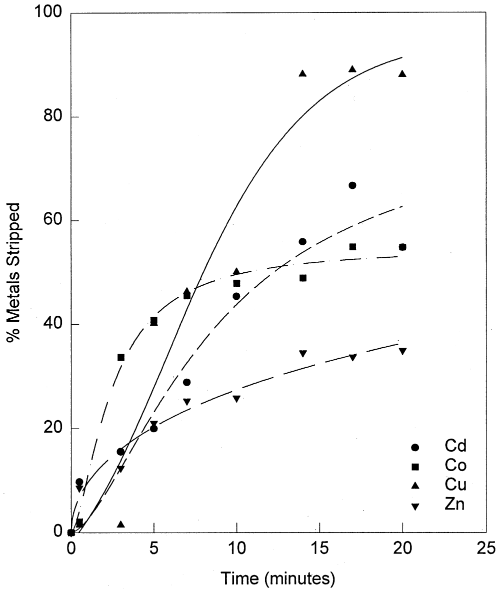

Figure 5. Stripping of 100 ppm each of cadmium, cobalt, copper and zinc, in 0.3M DEHPA simultaneously with 0.003M EDTA solution using hollow fiber membrane module (EDTA is limiting).

tion of each metal ion was increased to 100 ppm while the EDTA concentration remained constant. The percent metal ion stripped versus time is shown in Figure 5, and the results are summarized in Table 1, Run#2. It can be seen that the percent of metal ions stripped decreased to about half for each metal ion. This shows that the amount of EDTA used in this run is limiting to the amounts of metal ions to be stripped from aqueous feed solution to the EDTA receiving solution via non-dispersive LLE and LLBE in hollow fiber membrane modules.

Two more experiments were conducted to check if there was any interference between the metal ions. In Run #3, the EDTA concentration was increased to 0.012 M. The metal ion concentrations were the same as for Run #2. The stripping results are summarized in Table 1, Run #3. In Figure 6, the percent stripping of metal ions as a function of time is shown for Run #3.

In Run #4, the concentration of EDTA was reduced to 0.006M, while that of the metal ions was maintained constant at 100 ppm to give the theoretical concentration of metal ions required for the stripping. Figure 7 shows the percent stripping of metal ions as a function of time, and the results are summarized in Table 1, Run #4. Figures 6 and 7 are very similar to Figure 4. Since the % of metal ions stripped did not decrease, it can be conclude that there was no significant interference between the metal ions in the non-dispersive LLBE.

Table 1. Stripping of Cd, Co, Cu and Zn Simultaneously from 0.3M DEHPA Solution with EDTA Using Hollow Fiber Membrane Modules

Experimental Conditions

Room Temperature:	~ 25°C
Aqueous Feed Side Pressure: 14.7 psia	Flow Rate: 78 ml/min
Organic Phase Side Pressure: 16.5 psia – 16.7 psia	Flow Rate: 78 ml/min
Strip Solution Side Pressure: 17.7 psia	Flow Rate: 77 ml/min

Run #*	Cd (ppm)	% Cd stripped	Co (ppm)	% Co stripped	Cu (ppm)	% Cu stripped	Zn (ppm)	% Zn stripped
Run #1	19.21	76.78	15.93	63.47	23.16	92.60	13.76	55.89
Run #2	54.77	54.84	54.77	54.77	87.99	87.70	34.98	34.92
Run #3	77.86	77.96	64.33	64.33	92.89	92.58	53.96	53.87
Run #4	76.33	76.43	62.85	62.85	88.90	88.61	54.90	54.81

* EDTA Concentrations (Molar)

Run #1: [EDTA] = 0.003 M
Run #2: [EDTA] = 0.003 M
Run #3: [EDTA] = 0.012 M
Run #4: [EDTA] = 0.006 M

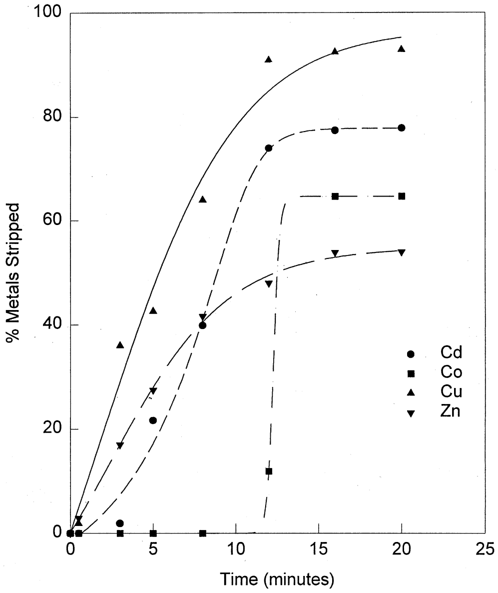

Figure 6. Stripping of 100 ppm each of cadmium, cobalt, copper and zinc, in 0.3M DEHPA simultaneously with 0.012M EDTA solution using hollow fiber membrane module.

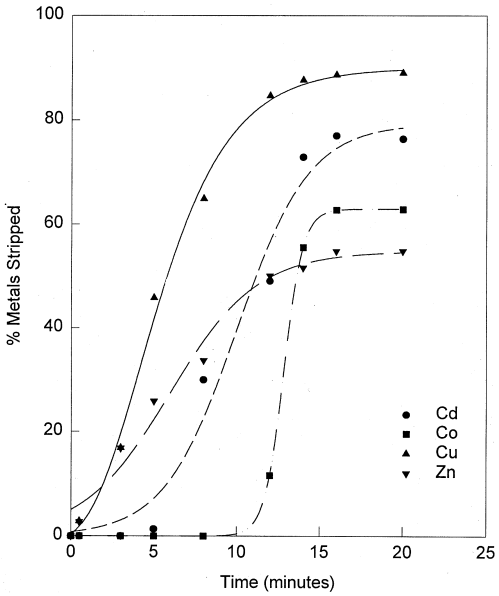

Figure 7. Stripping of 100 ppm each of cadmium, cobalt, copper and zinc, in 0.3M DEHPA simultaneously with 0.006M EDTA solution using hollow fiber membrane module.

CONCLUSIONS

The results obtained show EDTA can be used to back-extract Zn(II), Cu(II), Co(II) and Cd(II) from organic DEHPA solution via non-dispersive LLE/LLBE. Based on preliminary experimental data, the following conclusions are made:

- EDTA can be used to strip more than 55% of cadmium, cobalt, copper and zinc from DEHPA in batch experiments using equilibrium LLE.
- Using 100% recycle in the hollow fiber membrane experiments, the two polysulfone membrane modules (one for extraction and the other for stripping) can extract and strip cadmium, cobalt, copper and zinc simultaneously and achieve comparable results with that in the batch experiments.
- There was no significant interference between the metal ions when they were stripped with EDTA from DEHPA.

Thus, the two-membrane module hollow fiber system provides an alternative to conventional liquid-liquid extraction for extraction and recovery of metal ions from aqueous solution via a non-dispersive process. In particular, the proposed scheme may find application in waste treatment where a high ratio of waste stream/stripping solution desirable.

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