CHAPTER III

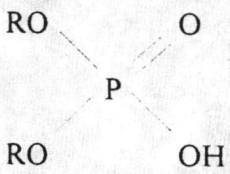
THE COBALT EXTRACTION EXPERIMENTS

This chapter presents the system configurations together with the experimental procedures for cobalt extraction from aqueous solutions using oxalic acid and hydrochloric acid solutions as strip solutions. All the materials used in the experiments are summarized in Table 3-1.

Table 3-1 The materials used in the experiments

Material	Chemical	Formula	Product of
Metal ion	Cobaltous chloride	$CoCl_2 \cdot 6H_2O$	Farmitalia Carlo Erba
Strip solutions	Hydrochloric acid	HCl	Merck
	Oxalic acid	$(COOH)_2 \cdot 2H_2O$	Ajax Chemicals
Basic reagent	Sodium hydroxide	NaOH	Eka Nobel
Extractant	Di-(2-ethylhexyl) phosphate	$C_{16}H_{35}O_4P$	Sigma Chemicals
Organic solvents	Toluene	C_7H_8	Merck
	N-dodecane	$C_{12}H_{26}$	Sigma Chemicals

The di-2-ethylhexyl phosphoric acid has the structure of



..... (3.1)

where the alkyl group (R) is $CH_3(CH_2)_3CH(C_2H_5)CH_2-$

Experimental Equipments

All the pH values were measured by using a pH meter, Model Accumet Basic, Denver Instrument Co. The concentration of cobaltous ion was measured by using atomic absorption spectrophotometer, Model IL551, AA/AE Spectrophotometer, Instrumentation Laboratory Inc. The other equipments used in the batch experiments and the HFSLM experiments were described below.

1. Batch Experiments

1.1 A 2-litre beaker

1.2 A stirrer of model RW20, Janke & Kunkel, equipped with a four-bladed 45-degree pitched impeller

2. Hollow Fiber Supported Liquid Membrane Experiments

2.1 The Liqui-Cel® Laboratory Liquid/Liquid Extraction System which is composed of two sets of gear pump of maximum flow rate 1 l/min, two variable speed controllers, two rotameters, and four pressure gauges

2.2 The Celgard® X-10 microporous polypropylene was used as a support material. The characteristics of the hollow fiber module are shown in Table 3-2

Table 3-2 The characteristics of the hollow fiber module

Characteristics	Specification
Inside diameter	240 μm
Wall thickness	30 μm
Effective pore size	0.05 μm
Porosity	30%
Number of fibers	240
Effective surface area	1.4 m^2
Effective area/volume	29.3 cm^2/cm^3
Effective volumetric flowrate	0.95–14 l/min
Module dimension (DxL)	8×28 cm (2.5×8 in)
Maximum transmembrane differential pressure	4.1 bar (60 psi)
Maximum operating temperature range	1 °C to 60 °C

Experimental Procedures

1. Batch Experiments

The equilibrium constants for cobaltous-ion extraction (K_{ex}) at two acidicities and the equilibrium constants for cobaltous-ion stripping (K_{st}) with two types of acid serving as strip solutions were studied in three batch experiments.

1.1 The first batch: using oxalic acid as a strip solution

1.1.1 The feed solution was 10,000 ppm of cobaltous ion with pH about 5, and 250 ml in volume.

1.1.2 The organic solution was 20 V/V% D2EHPA in toluene, and the total volume of 250 ml.

1.1.3 The strip solution was oxalic acid solution with pH about 1.4, and volume of 250 ml.

1.1.4 First, the feed solution was stirred with the organic solution at the speed of 500 rpm. The feed solution was periodically sampled and its pH values were measured. The extraction experiments were carried on until the pH values of the raffinate were constant.

1.1.5 Then, the organic solution which contained cobalt complex was separated from the mixture in 1.1.4.

1.1.6 The solution obtained from 1.1.5 was mixed with the strip solution. The strip solution was also sampled periodically and its pH values were measured. Like the extraction experiments, the stripping experiments were stopped when the pH values were constant.

1.2 The second batch: using hydrochloric acid as a strip solution

The procedure was the same as in the former except (1.1.3) the strip solution used was hydrochloric acid solution with pH 1.4.

1.3 The third batch: using hydrochloric acid as a strip solution

The procedure was the same as in the second except the pH of feed solution was adjusted to 6.5 by adding small quantity of 2M NaOH.

The conditions for batch experiments of cobaltous ion extraction were summerized in Table 3-3.

Table 3-3 The experimental conditions for cobalt extraction batch experiments

Batch / Condition	I	II	III
The type of strip solution	Oxalic acid	Hydrochloric acid	Hydrochloric acid
The pH of strip solution	1.47	1.57	1.35
The pH of feed solution	4.99	4.80	6.56
The cobalt concentration in feed solution	10,060	12,002	11,880

2. Hollow Fiber Supported Liquid Membrane Experiments

2.1 First, the 250 ml of organic solution containing D2EHPA was circulated in the tubeside of fibers for 10 minutes.

2.2 Both the feed and strip solutions were presaturated with some amount of the organic solution left from impregnation.

2.3 Then the experiment was started by flowing, in the tubeside, the feed solution of which pH was adjusted by adding some amount of sodium hydroxide solution. Simultaneously, the strip solution was pumped into the shellside countercurrently.

2.4 For circulating-mode operation, the experiments were stopped when steady state was reached, observed from the constant flow meters and pressure gauges.

2.5 For once-through-mode operation, as the feed solution passed the module, the pH was dropped drastically. Hence, some amount of sodium hydroxide was added into the raffinate to adjust the pH in order to be used as the feed solution for the next stage. Again, both feed and strip solutions were pumped into the module in the same manner.

Figure 3-1 shows the Liqui-Cel Laboratory Liquid/Liquid Extraction System equipped with the Liqui-Cel Membrane Contactor used in the HFSLM experiments. For a schematic representation of the structure of Liqui-Cel Membrane Contactor, see Appendix D.

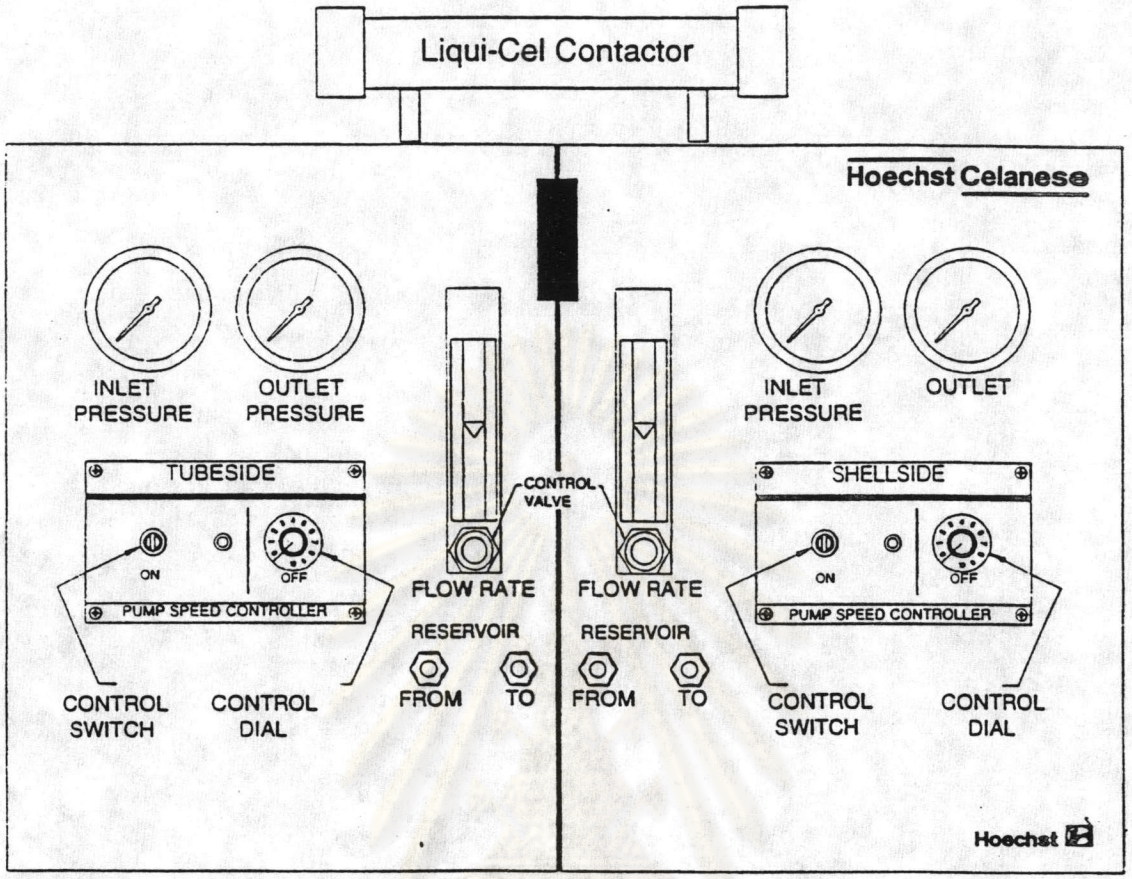


Figure 3-1 The Liqui-Cel Laboratory Liquid/Liquid Extraction System equipped with the Liqui-Cel Membrane Contactor

The schematic countercurrent flow diagrams for circulating-mode operation and for once-through mode operation in HFSLM experiments are shown in Figure 3-2 and Figure 3-3, respectively.

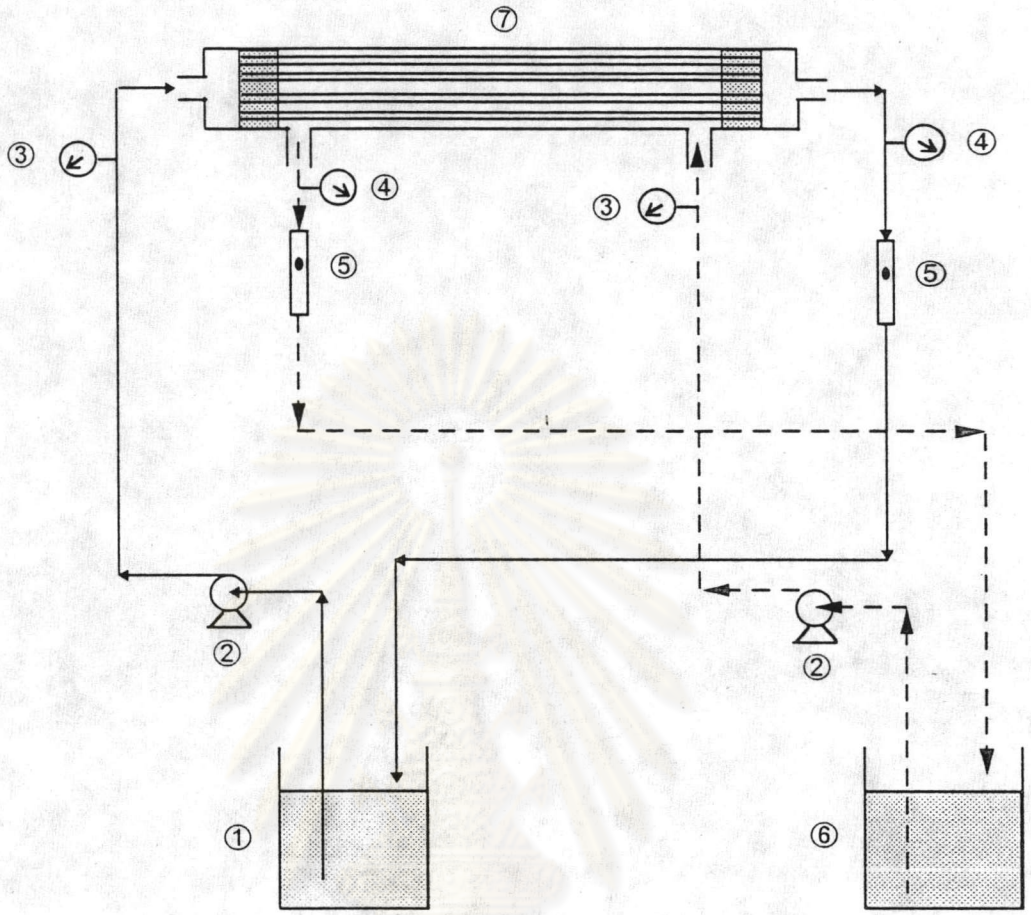


Figure 3-2 Schematic countercurrent-flow diagram for circulating-mode operation in HFSLM experiments where ① the feed reservoir, ② gear pumps, ③ inlet pressure gauges, ④ outlet pressure gauges, ⑤ flow meters, ⑥ the strip reservoir, and ⑦ the HFSLM contactor

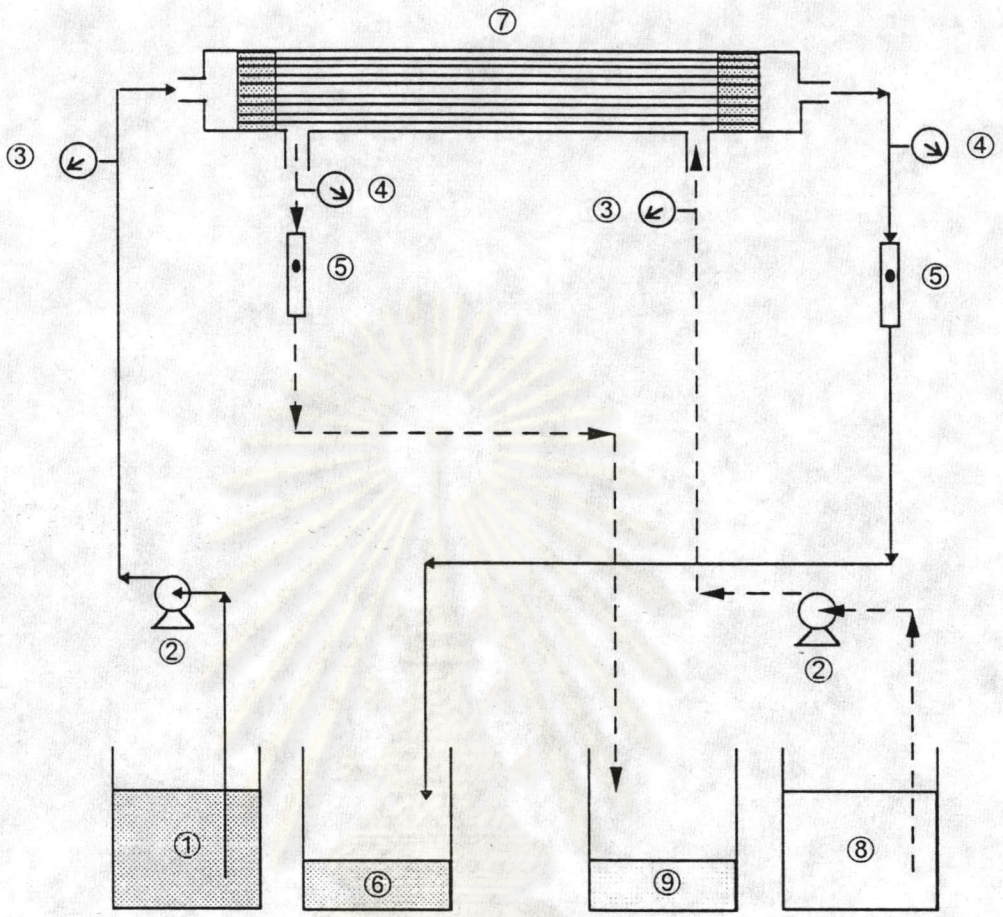


Figure 3-3 Schematic countercurrent-flow diagram for once-through-mode operation in HFSLM experiments where ① the feed solution reservoir, ② gear pumps, ③ inlet pressure gauges, ④ outlet pressure gauges, ⑤ flow meters, ⑥ the raffinate reservoir, ⑦ the HFSLM contactor, ⑧ the strip solution reservoir, and ⑨ the concentrated solution reservoir

The Objectives of the Research

The experiments were performed with the following objectives:

1. To explore the possibility of extracting cobalt from aqueous solutions by applying a hollow fiber supported liquid membrane process.

2. To study the factors which affect the extraction of cobalt from aqueous solutions by this process. The factors studied can be divided into two groups:

2.1 The variables

2.1.1 The concentration of cobaltous ion in feed solution

2.1.2 The pH of feed solution

2.1.3 The volumetric flowrates of both feed and strip solutions

2.1.4 The concentration of D2EHPA in organic solution

2.2 The parameters

2.2.1 The types of strip solution

2.2.2 The types of organic solvent

2.2.3 The modes of operation

The Scope of the Research

The extraction of cobaltous ions from aqueous solutions by the hollow fiber supported liquid membrane process was studied according to the following conditions:

1. The concentrations of cobaltous ion in feed solution were 5,000, 8,000, and 10,000 ppm.
2. The pH of the feed solutions were 4, and 6.5.
3. The types of strip solution were oxalic acid and hydrochloric acid solutions.
4. The modes of operation were once-through and circulating mode.
5. The volumetric flowrates of both the feed the strip solutions were 100, 500, and 1,000 ml/min.
6. The concentrations of D2EHPA used as an extractant in toluene were 10, 15, 20, and 25 V/V%.
7. The types of organic solvent were toluene and n-dodecane.

All the experiments were carried out at room temperature.