

***SELECTIVE RECOVERY OF CADMIUM (II)
IONS FROM INDUSTRIAL WASTE
EFFLUENTS USING SUPPORTED LIQUID
MEMBRANES***

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OUTLINE

- Sources of Cd(II) in the Environment
- What is a SLM?
- Mechanism of transport through SLM
- Membrane reactors
- Applications
- Membrane Stability
- Comparison with conventional solvent extraction

Sources of Cd(II)

- Natural occurrence in air, water and soil
- Drilling Fluids
- Produced Formation Water
- Leach into water bodies from pipes and solder
- Electrode component in alkaline batteries
- Paint pigments
- Anti-corrosive coatings
- Manufacturing of electronic components
- Select metal alloys

What is a SLM?

SLM consists of a solution, in a water immiscible low dielectric constant solvent, of an extracting agent absorbed on a thin microporous support

Microporous Supports

A thin polymeric film, made up of a hydrophobic material with defined porosity

Materials: Polypropylene, polysulphones, PTFE etc

Pore size : 0.02-0.6 μm

Thickness : 25-30 μm

Porosity : 35-50 %

Carriers

Reagents that are impinged onto the solid supports are termed as carriers. e.g TBP, 2EHPA, Alamine 336, TOA, Crown Ethers etc

Diluents

Diluents are used to reduce the viscosity of the system. Commercial kerosene, n-decane, dodecane, xylene etc

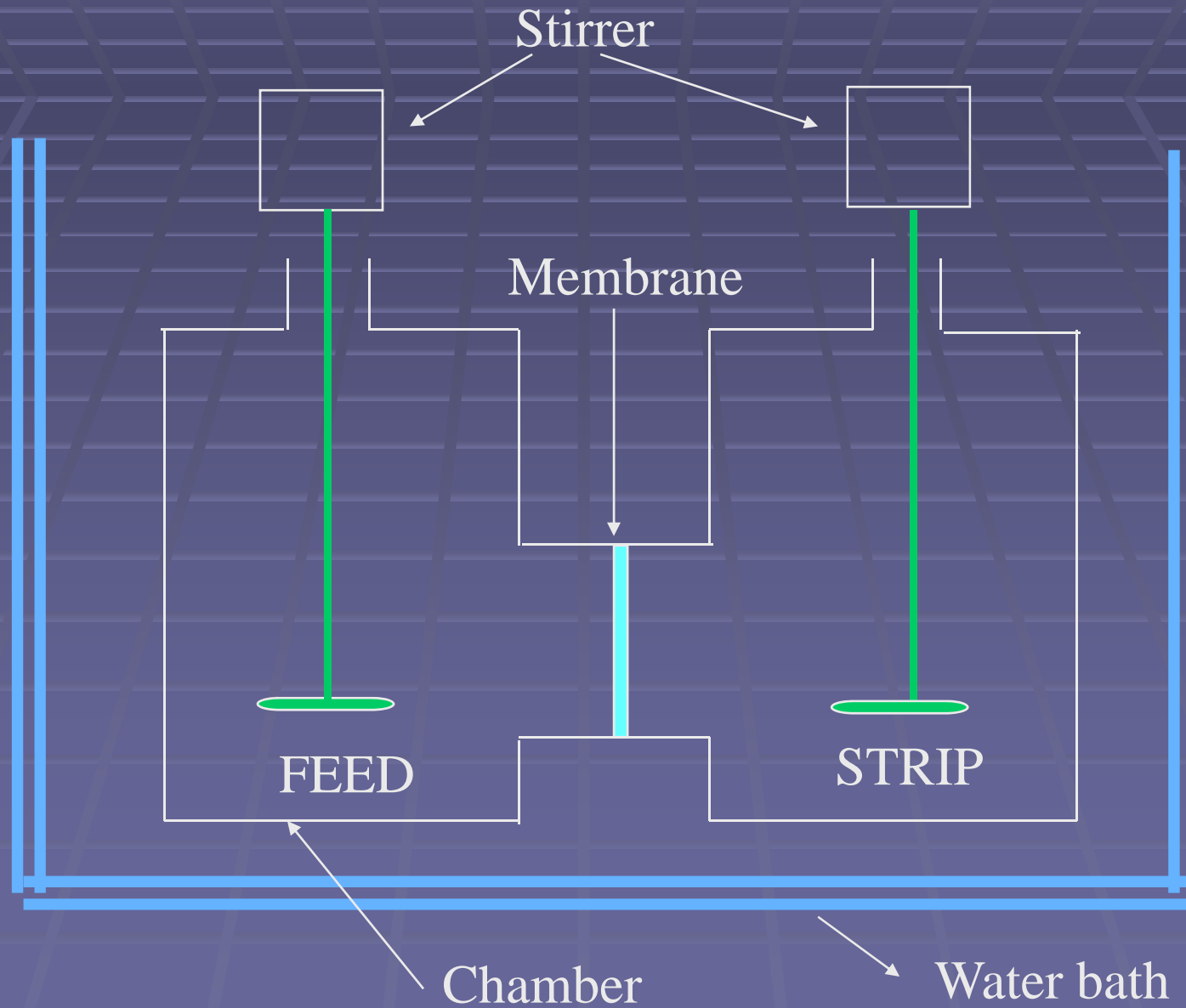
Feed & Strip Solutions

*The aqueous solution initially containing all the metal ions which can permeate the SLM, is referred to as **feed solution**, where as the aqueous solution present on the opposite side of the membrane, which is initially free from permeable metal ions, is referred to as **strip solution***

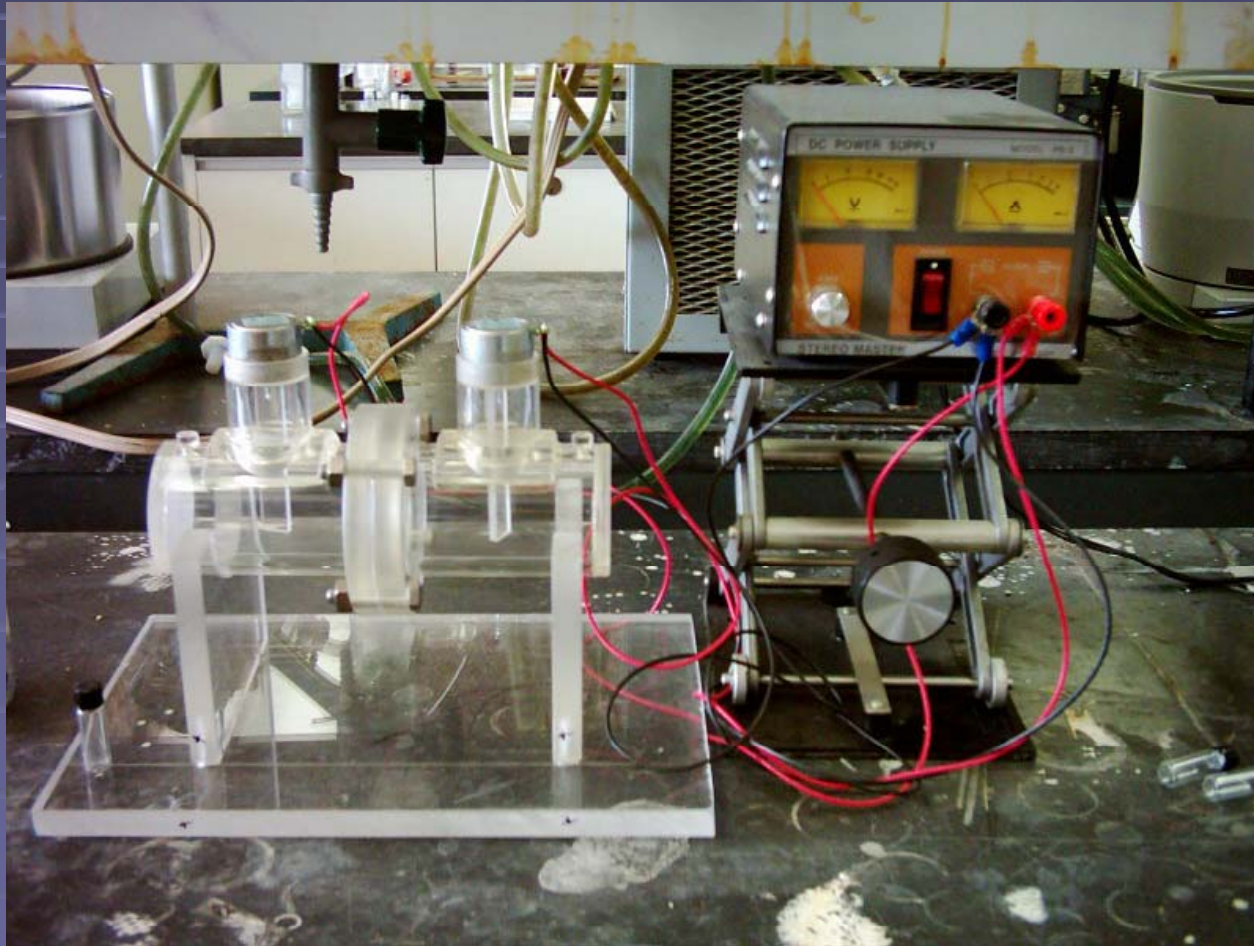
Salient features of SLM

- 1. High selectivity*
- 2. Ions can be pumped “uphill”*
- 3. Fluxes are higher than with solid separators*
- 4. Low capital and operating costs*
- 5. Expensive “tailor-made” extractants can be utilized with economy*
- 6. High separation factors are achieved in a single stage*
- 7. High feed/strip volume ratios*

Membrane Reactor



Membrane Reactor



Studies on Transport of Cd(II)

Carrier: *Triethanolamine in Toluene*
Feed: *Aqueous Cd(II) solution*
Strip: *0.1M NaOH solution*

Physical Properties of membranes

Membrane	Pore size (um)	Thickness (um)	Porosity (%)	Material
Durapore	0.20	125	75	PVDF

Membrane

Reactor: Each half Cell: 140 cm^{-3}
Membrane effective area: 14.2 cm^{-3}
Stirring: 1000 rpm
Temperature: $25 \pm 1^\circ \text{C}$

$$\frac{C}{C_0} = -\frac{Q}{V} Pt$$

Flux Equations

$$J = -\frac{dC}{dt} \frac{V}{A}$$

$$\ln C_f = -\frac{AK_f}{V_f} t + C$$

- where J is flux, V_f is the volume of the feed solution, A is the membrane area in contact with the aqueous solution and C is concentration of analyte at any time t , K_f is mass transfer coefficient

How to prepare membrane

TWO METHODS:

1. *Impregnation by Immersion*

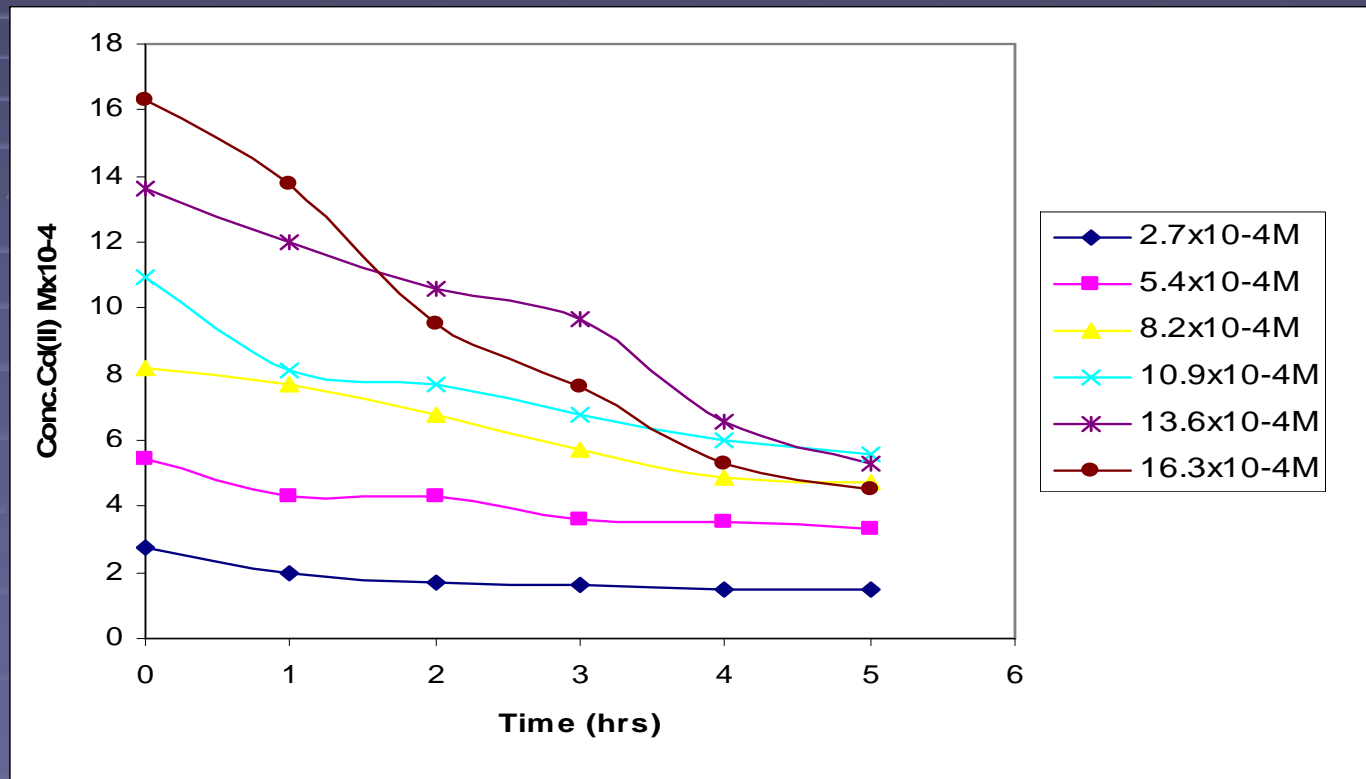
Support is immersed in organic phase at room T & P for varying time.

2. *Impregnation under vacuum*

Air contained in pores of solid support or dissolved in organic phase is removed and impregnation is made under vacuum.

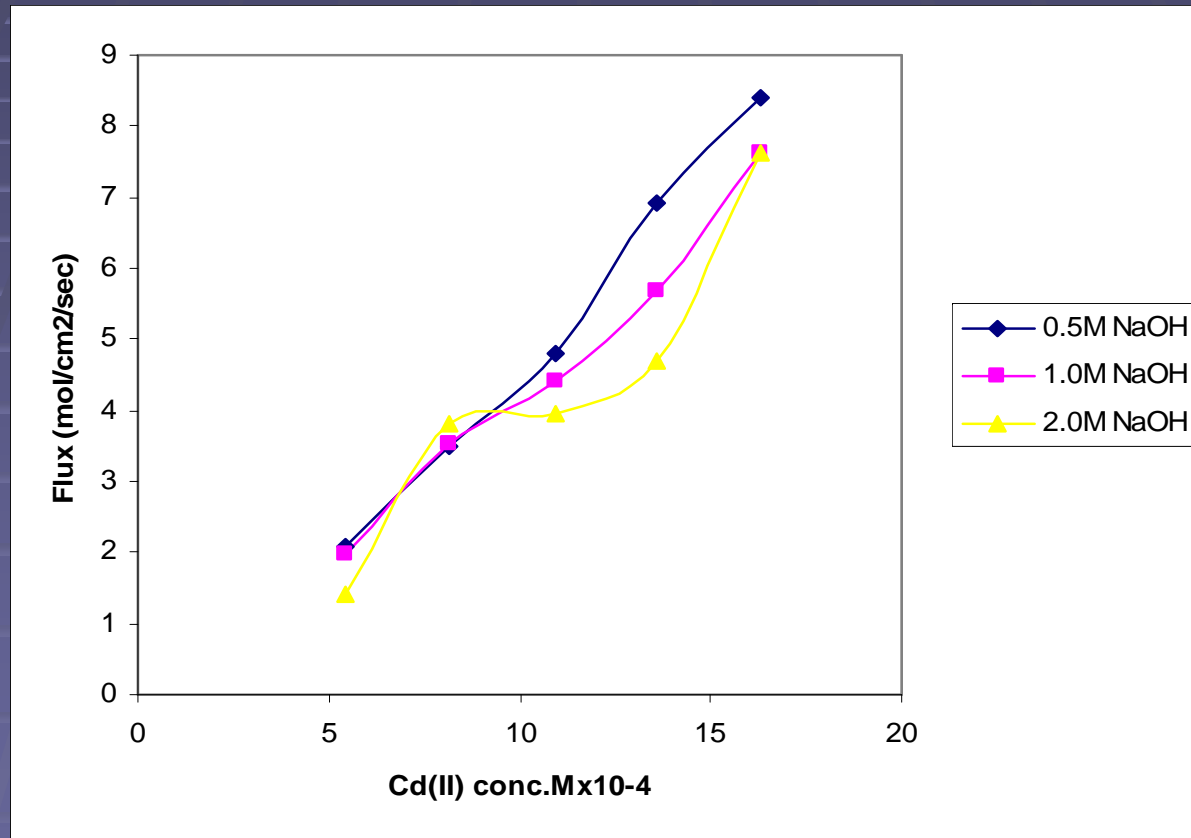
Decrease in Cd(II) ions concentration in feed vs. time.

Effect of feed concentration

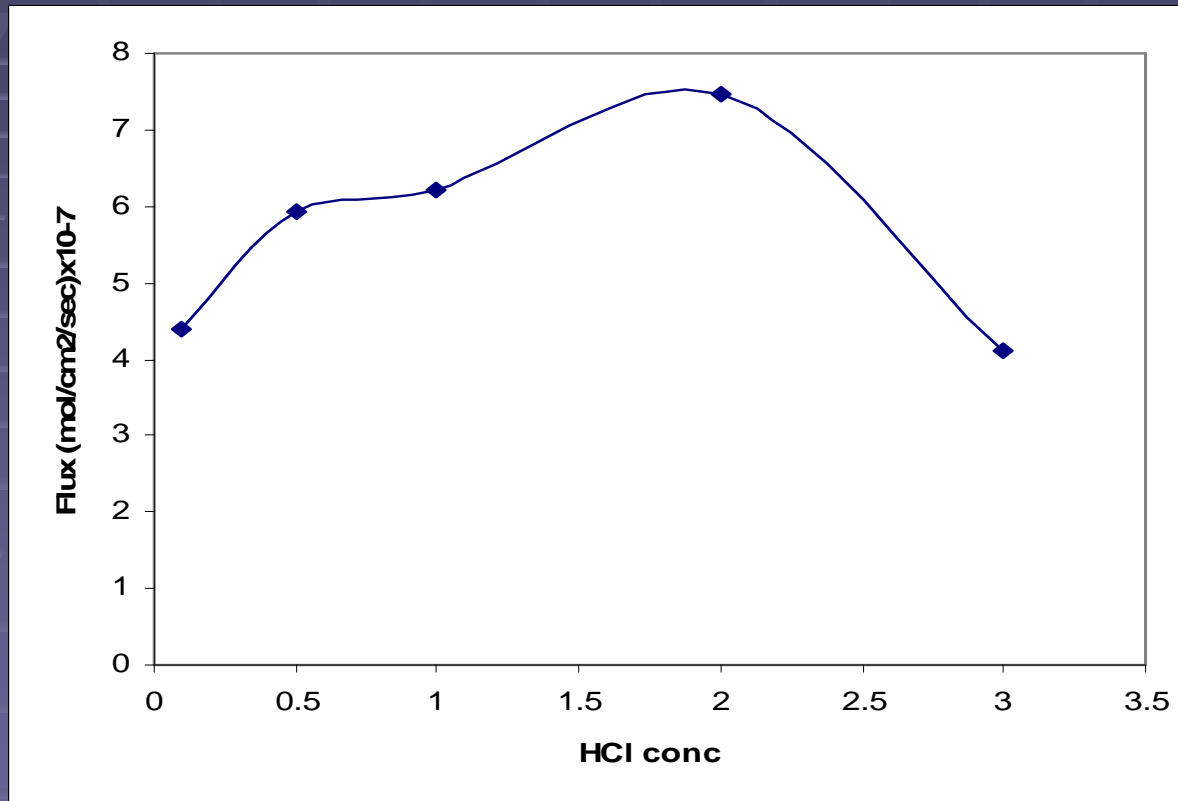


Effect of Cd(II) concentration on flux.

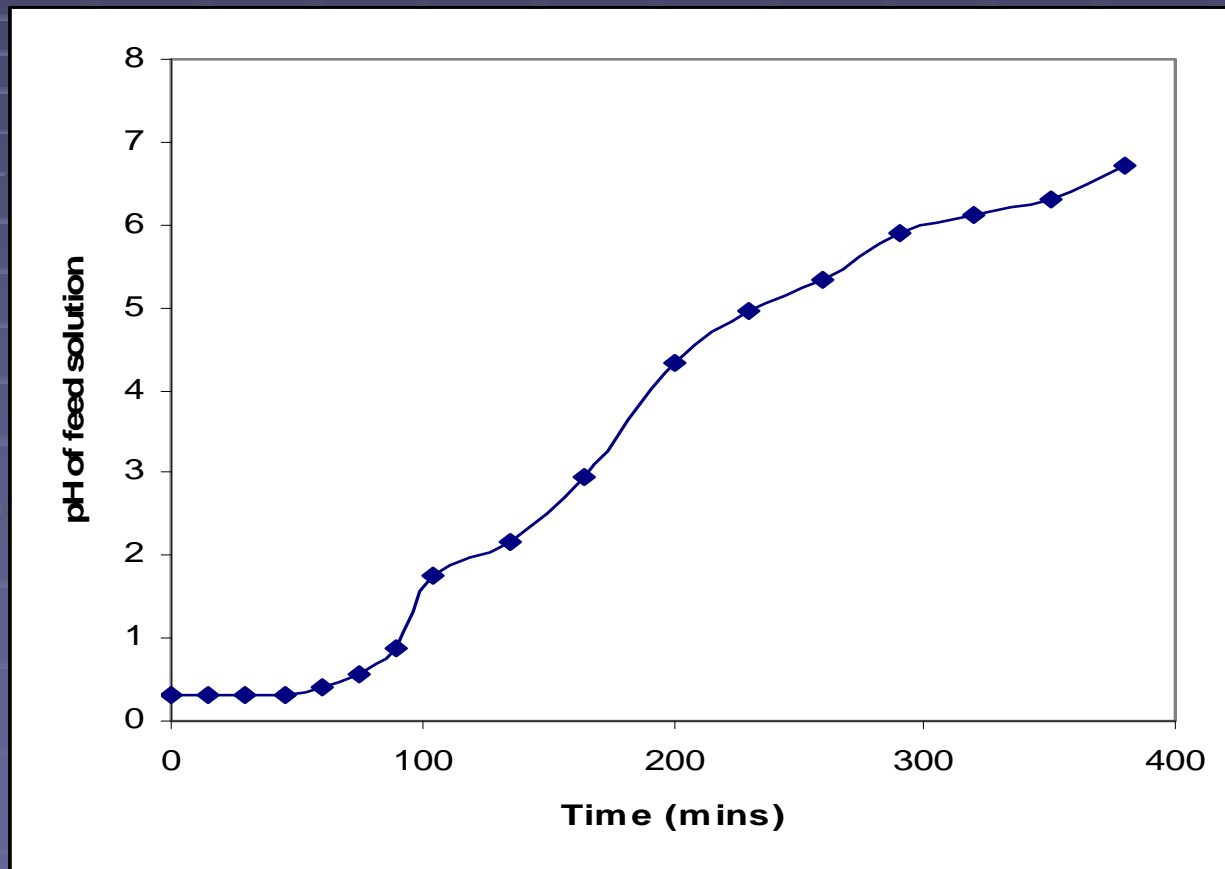
Effect of strip concentrations



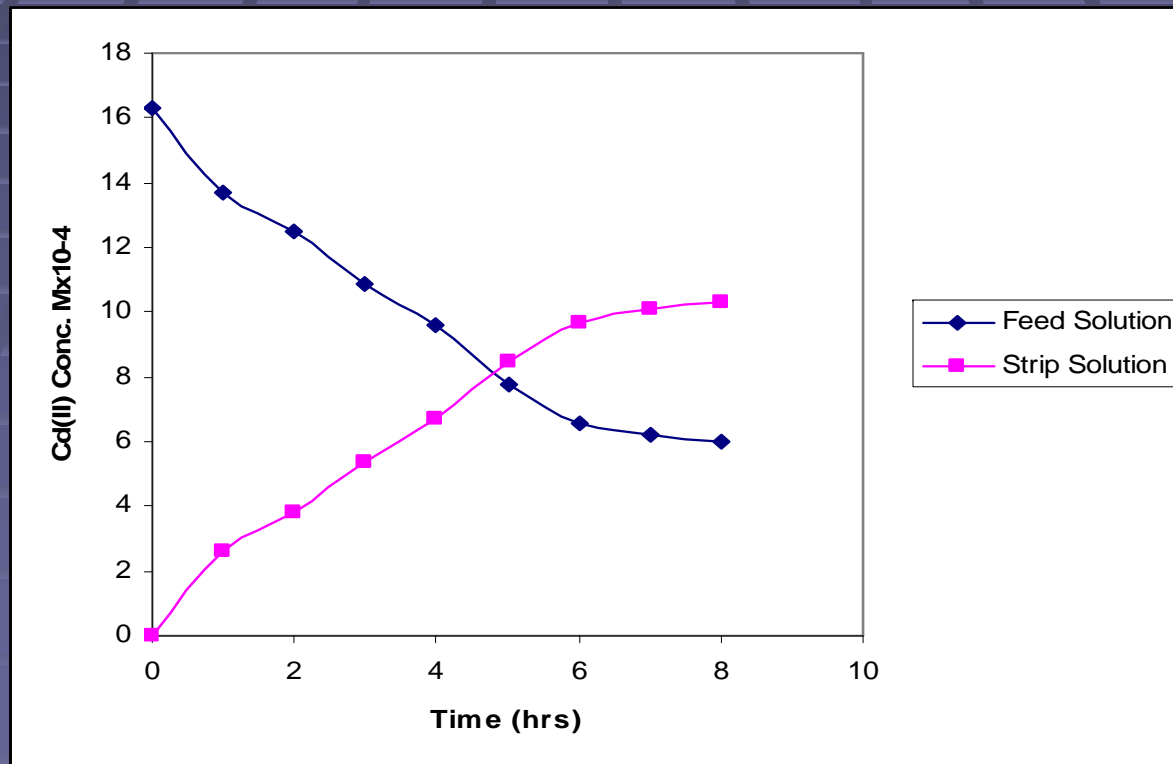
Effect of Cd(II) concentration on flux.
Effect of HCl concentrations in feed.



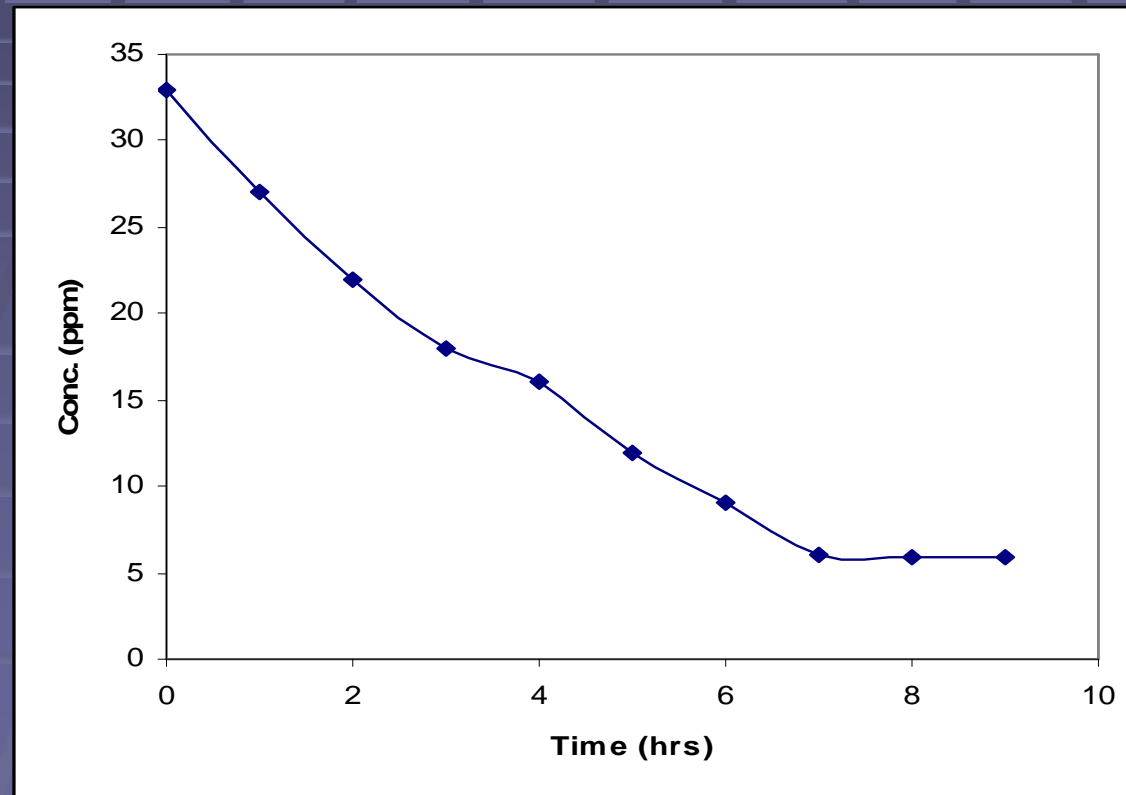
Variation of pH in feed solution vs. time.
[NaOH]=1.0M, [TEA]=3.0M, [HCl]=2.0M,
[Cd(II)]= 16.3×10^{-4} M



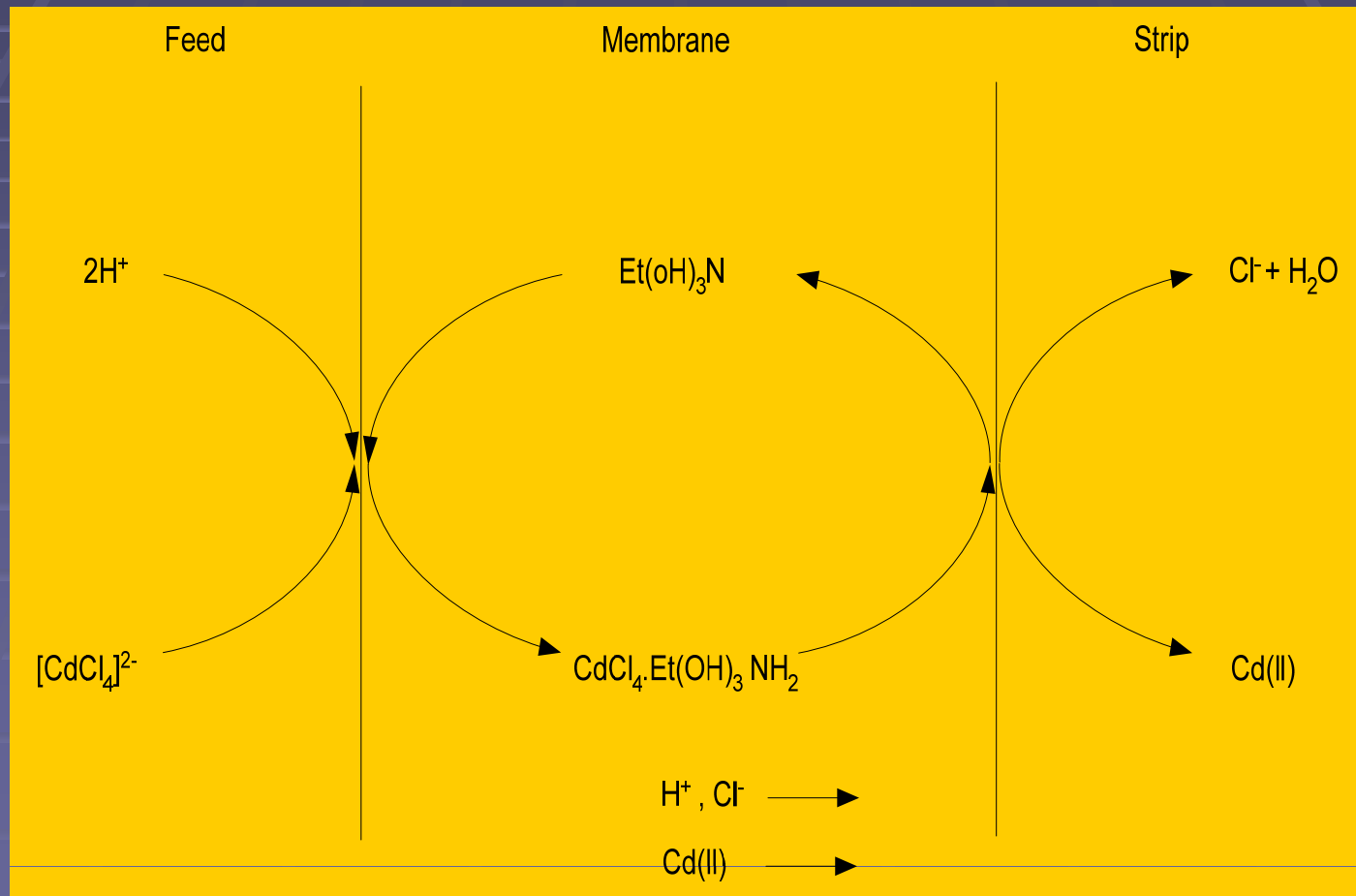
Cd(II) concentration in feed and strip solutions vs. time with 0.05M EDTA solution in feed. [NaOH]=1.0M, [TEA]=3.0M, [HCl]=2.0M, [Cd(II)]= 16.3×10^{-4} M



Decrease in concentration of Cd(II) ions in feed vs. time for aqueous effluent. [NaOH]=0.5M, [TEA]=3.0M, [HCl]=2.0M, [Cd(II)]=33ppm



Coupled co-ion transport of Cd(II) ions



Increasing Throughputs

By increasing effective surface area of the membrane, high throughputs can be achieved and bigger volumes of waste can be treated.

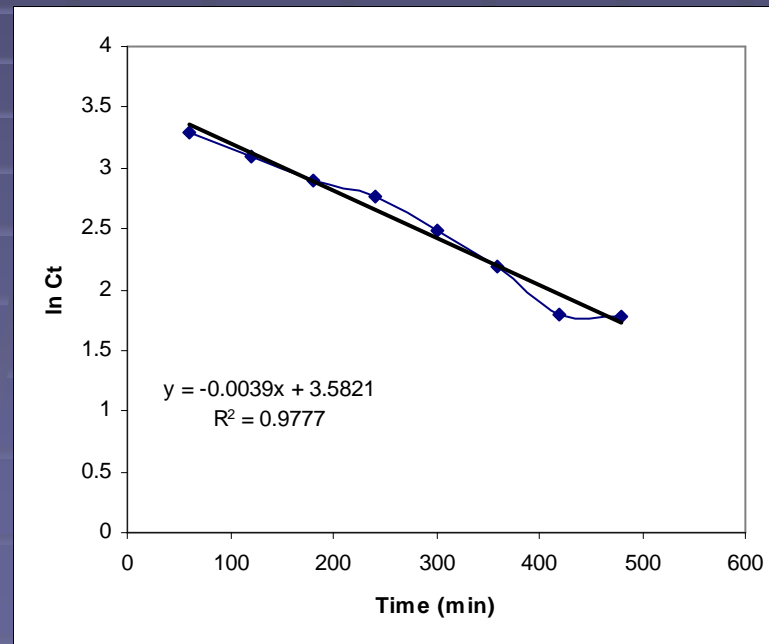
Three types of configurations;

- | | |
|------------------|---|
| 1. Spiral | 25-50 m ² -m ³ |
| 2. Plate & Frame | 400-600 m ² -m ³ |
| 3. Hollow Fiber | 600-1200 m ² -m ³ |

Typical Module: L=5.5in; id=240um; od=300um; Porosity=40%

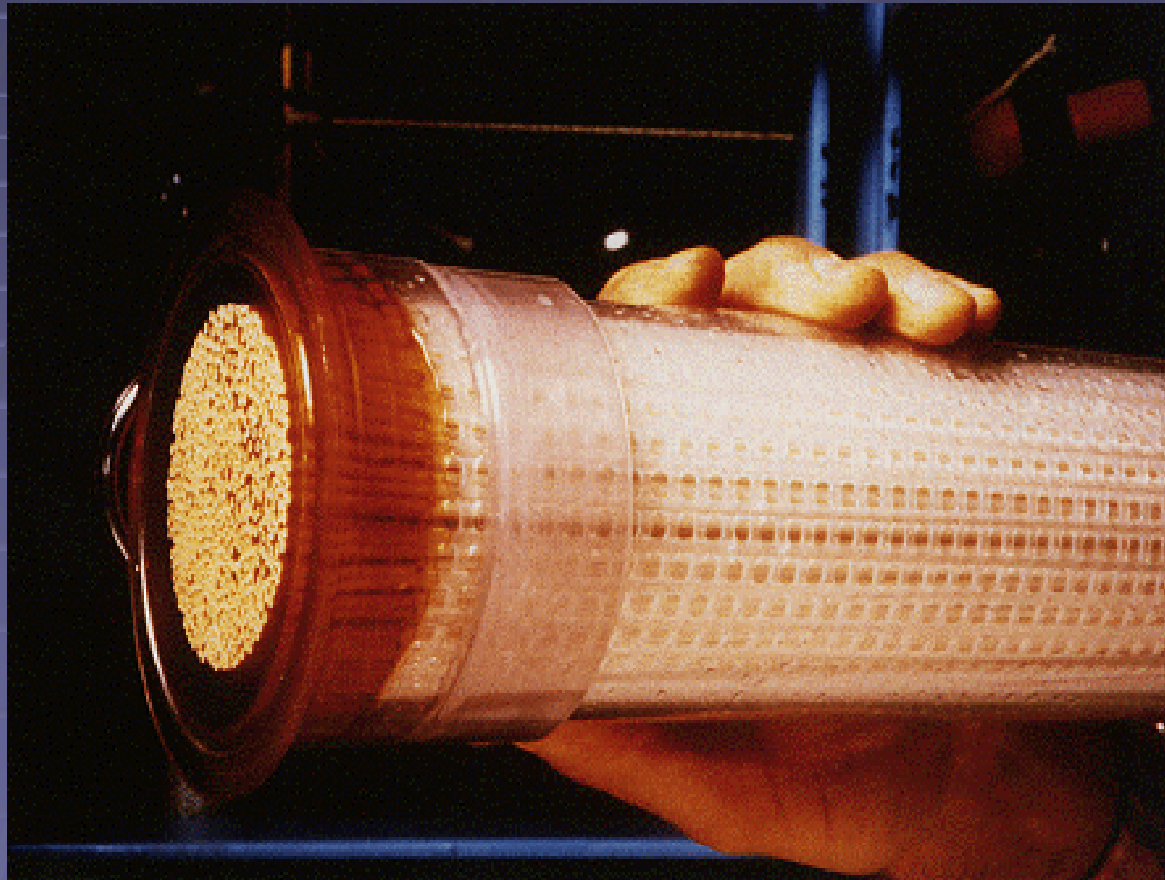
Utility of Mass Transfer Coefficient to increase throughput

Calculated value of K_f was 6.4×10^{-4} cm/sec



- About 35 ppm Cd(II) solution took about 7 hours to be reduced up to 6 ppm. It means about 6 times reduction in feed cadmium concentration was achieved. To increase the membrane surface area, a hollow fiber module was used with specifications as under;
- Membrane module: Type LiquiCel Hollow Fiber
- Membrane type: Polypropylene impregnated with TEA, OD/ID 300 μ m/220 μ m
- Membrane area: 650 cm²
- Feed Solution: 1 L wastewater ; Strip Solution: 100 mL 0.5M NaOH; Recirculation flow rate: 300 mL/min. Temperature: 25°C.
- If the same volume is treated with this assembly (as in the flat sheet cell) it will take only 40 minutes to reach from 34 ppm to 6 ppm in the feed. However, high volumes are encountered in actual situations. These data can be used to upgrade the lab. scale studies to handle large volumes of waste in given time. With HF module used, 1000 mL of waste water took 1 hour to be free from Cd(II) ions.

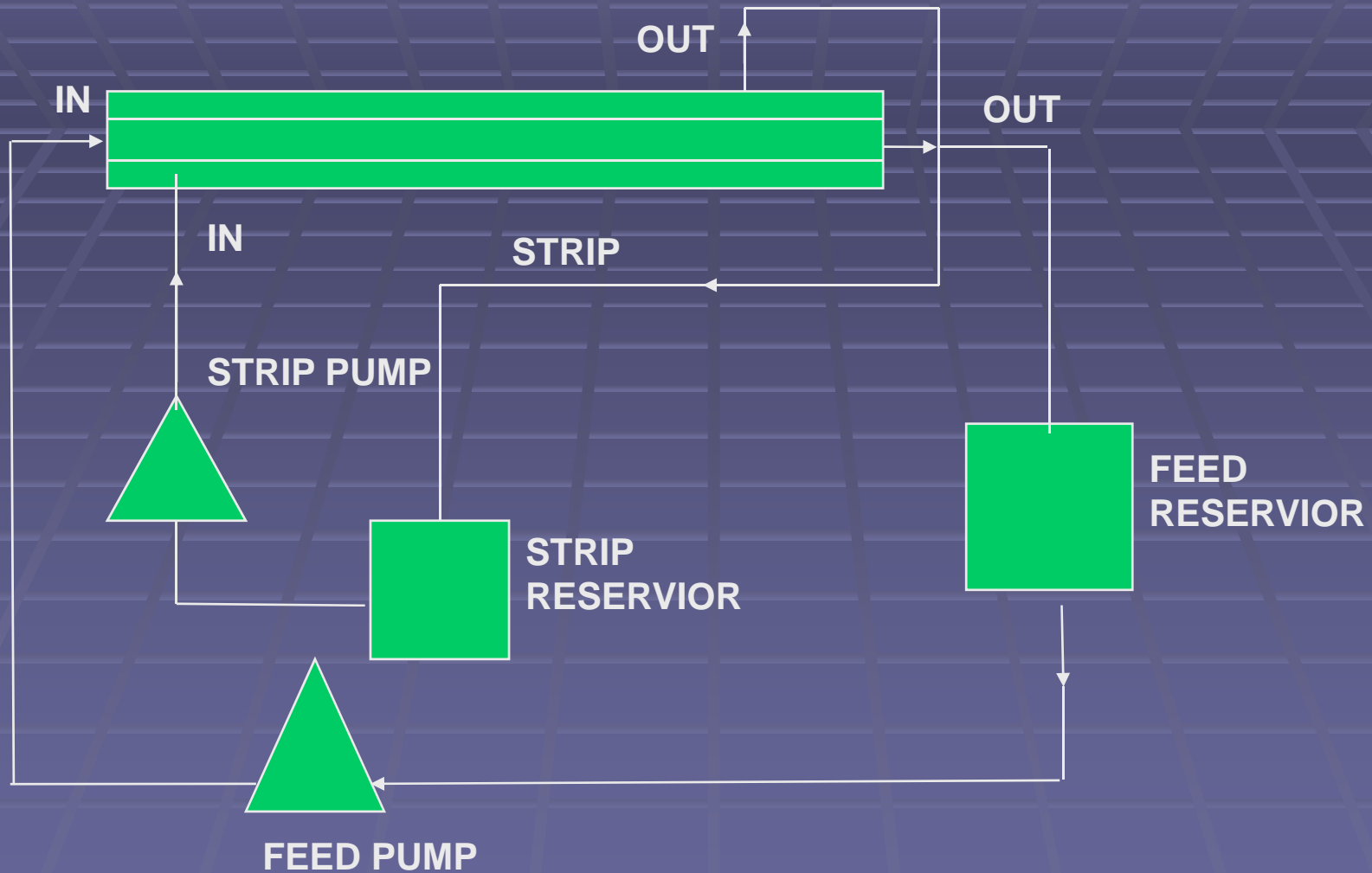
Hollow Fibers packed in a Module



Hollow Fibers in a Module

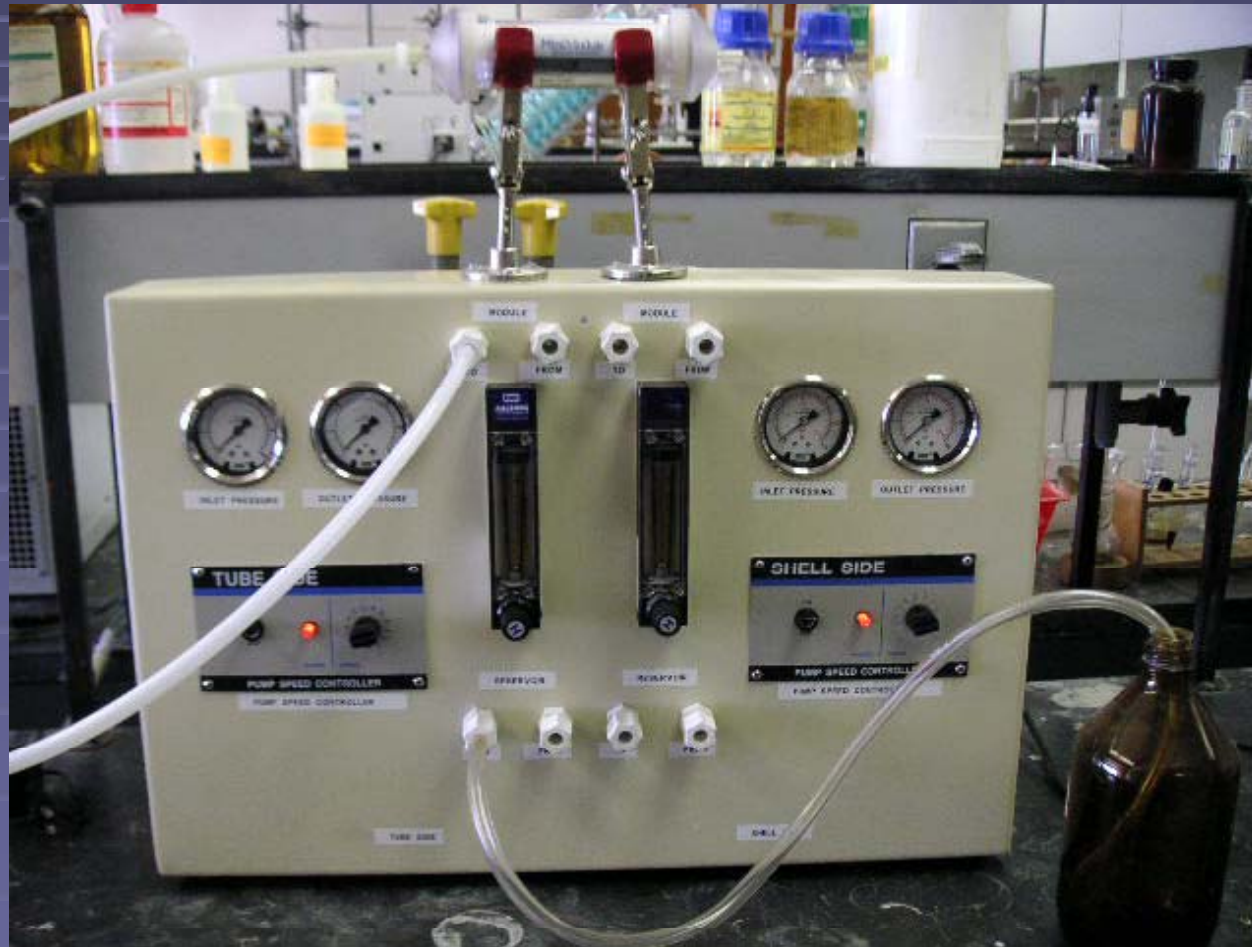


HF Module Assembly

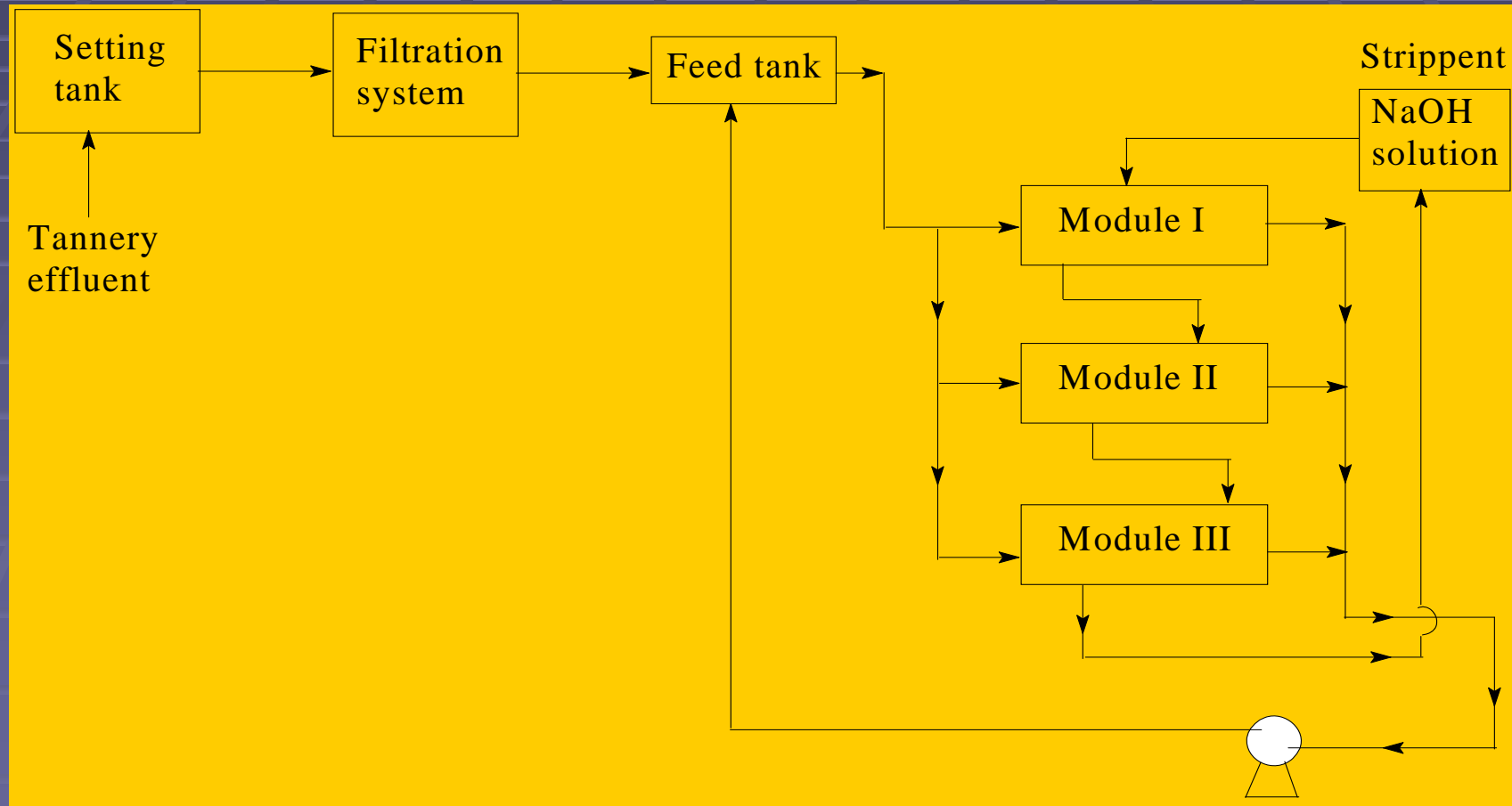


L=5.5in; id=240um; od=300um; Porosity=40%

LLE System



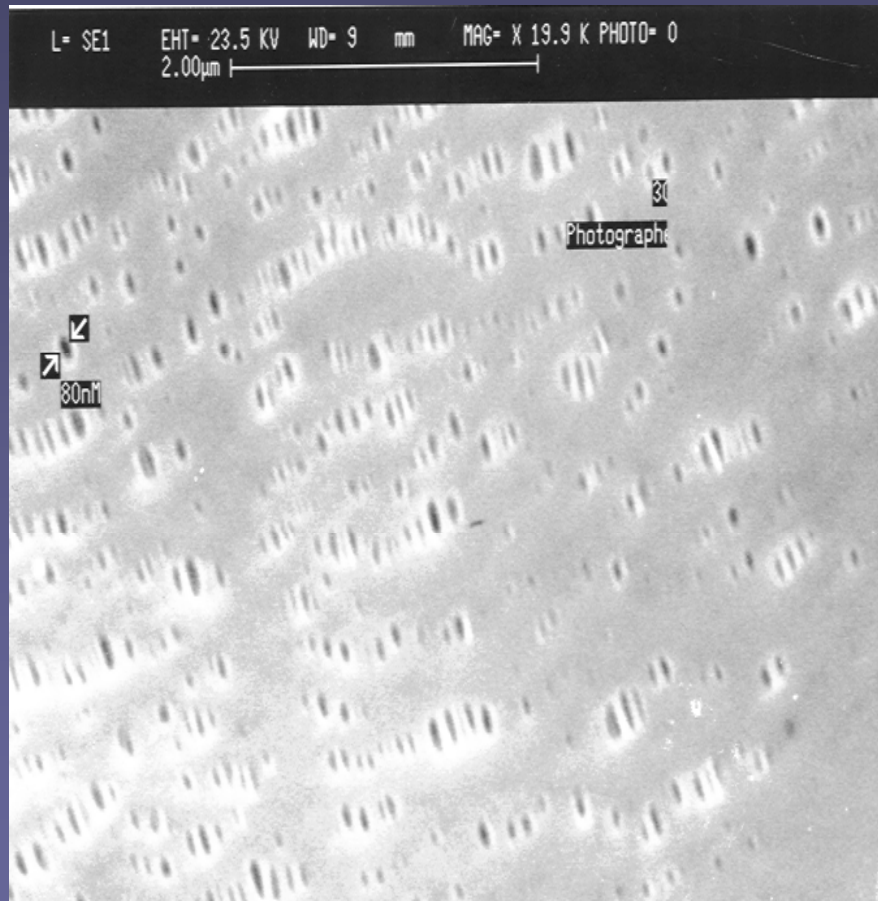
Schematic Upgradation



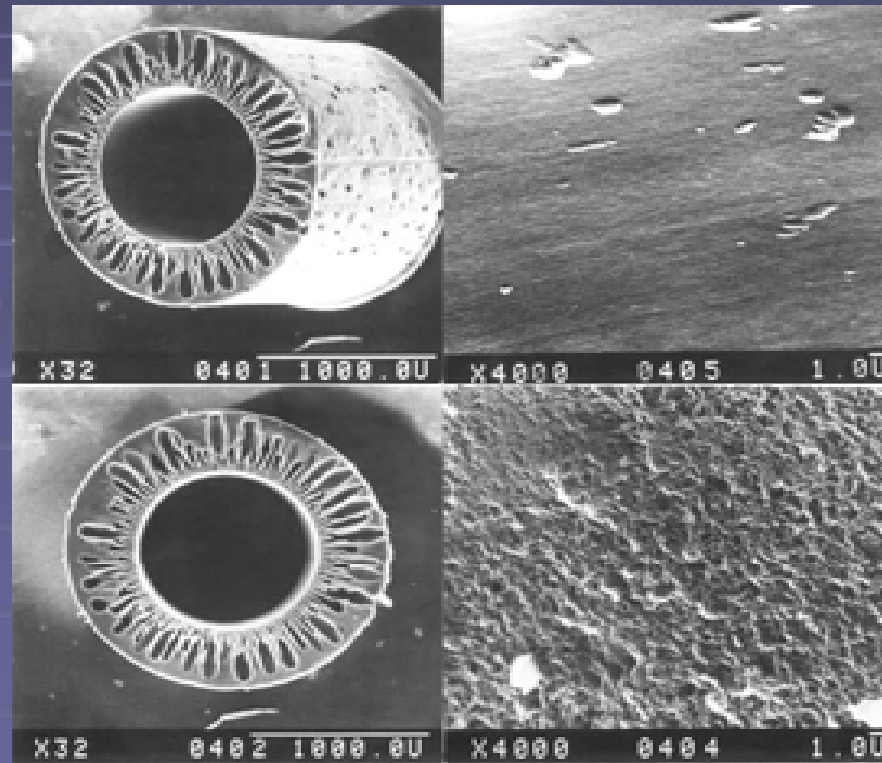
Pilot Plant



Scanning Electron Micrographs of the Membrane



Scanning Electron Micrograph of HF



■ **Conclusions**

- 1. The cadmium ions are transported across cyclohexanone membrane by coupled TEA-co-ion transport mechanism.
- 2. The optimum conditions of transport are 3.0M TEA in the membrane and 2.0M HCl in the feed.
- 4. Increase in Cd(II) concentration in the feed enhances the flux, so transport of Cd(II) ions are fast.
- 5. EDTA molecules also help to form complexed Cd(II) ions and facilitate the transport of this metal ions.
- 7. Larger volumes of waste can be handled with HF
- 6. TEA is a useful carrier for cadmium extraction by using SLM systems.



Thanks For Your Attention

