

CHAPTER III

EXPERIMENTAL SECTIONS

3.1 Instruments and apparatus

3.1.1 Electrodialysis system

Electrodialysis Cell Unit (PCCell GmbH model: PCCell ED 64-4, Germany) consisted of cathode, anode, membrane stack and other component which was shown in Figure 3-1.

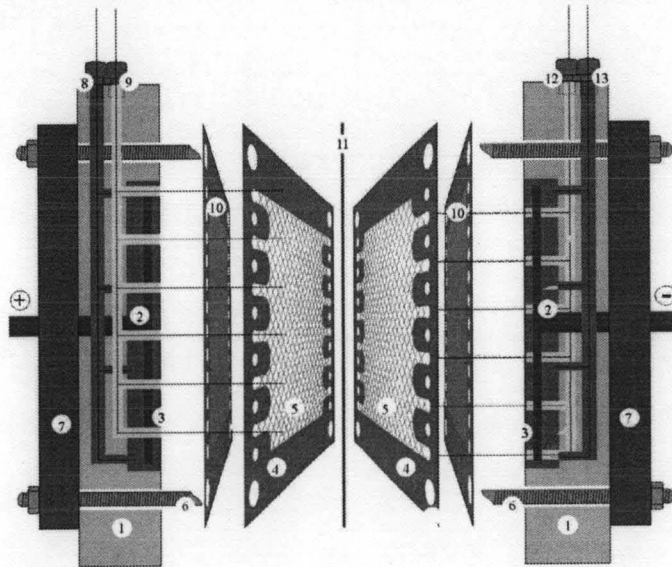


Figure 3-1 A diagram of the components of Electrodialysis Cell Unit (PCCell ED 64-4) [31].

Note:	1 = Polypropylene end plate	2 = Electrode
	3 = Electrode chamber	4 = Spacer sealing PVC
	5 = Spacer-fabric	6 = Screws
	7 = Stainless steel frame	8 = Inlet anode cell
	9 = Inlet concentrate cell	10 = Cation exchange membrane
	11 = Anion exchange membrane	12 = Inlet diluate cell
	13 = Inlet cathode chamber	

The electrode end plates consisted of anode and cathode. The description of the electrode end plates was shown in Table 3-1.

Table 3-1 Description of the electrode end plates

Item	Description
Cell frame	Polypropylene
Tubes	Polyethylene
Anode	Pt/Ir-coated Ti stretched metal
Cathode	Ti stretched metal

Note: Pt = Platinum, Ir = Iridium and Ti = Titanium

The membrane stack consisted of sulfonated polyether cation exchange membrane (CEM), quaternized ammonium polyether anion exchange membrane (AEM) and spacer. The characteristics and specifications of the membrane stack were shown in Table 3-2.

Table 3-2 Characteristics and specifications of the membrane stack

Item	Specification
Membrane type	Nonporous membrane
Membrane size	110 x 110 mm
Active membrane area	64 cm ² per membrane
Cell thickness	0.5 mm
Number of membranes	5 cell pairs
Spacer	Silicon/Polyester or Silicone/PVDF

Note: The membrane stack consisted of n cell pairs which were formed by n+1 cation exchange membranes, n anion exchange membranes and 2n spacers.

The apparatuses used with the electro dialysis system were

1. DC power supply (Yugo[®] model: YG3005D, Japan)
2. Magnet drive pump (Sanzo model: PMD-0311, Japan)
3. Liquid filter (LifeTech[®] model: AP1600)
4. PE Plastic tank 20 L
5. PE Plastic pipe 8 mm.
6. PE Plastic pipe ½"
7. HDPE reducing T connectors—continued ½" x 5/16" (Cole-Parmer International, USA.)
8. PP plastic ball valves (Two-way (straight)) ½" barb (Cole-Parmer International, USA.)

3.1.2 Flame atomic absorption spectrometer (FAAS) (Perkin-Elmer model: AAnalyst 100, USA.)

The operation conditions for analysis of Fe, Cr, and Ni were shown in Table 3-3.

Table 3-3 The operation conditions for FAAS

Operation conditions	Cr	Fe	Ni
Wavelength (nm)	357.9	305.9	232.0
Slit width (nm)	0.70	0.20	0.20
Lamp current (mA)	25	30	25
C ₂ H ₂ flow-rate (Lmin ⁻¹)	3	3	3
Air flow-rate (Lmin ⁻¹)	10	10	10

3.1.3 UV-Vis spectrophotometer (Hewlett Packard model: HP8453, USA.)

3.1.4 Glassware and apparatuses

1. Autopipette and tip 1000 μ L (Eppendorf, Germany)
2. Autopipette and tip 10 mL (Brand GMBH, Germany)
3. Graduate pipette 5 mL
4. Volumetric flasks 25, 50, 100 and 1000 mL (Pyrex[®], USA.)
5. Burette 50 mL (Pyrex[®], USA.)
6. Beakers 50, 100, 250, 600 and 1000 mL (Pyrex[®], USA.)
7. Erlenmeyer flask 125 mL (Pyrex[®], USA.)
8. Dropping bottle
9. Magnetic stirrer
10. Stirrer (Fisher scientific)
11. Desiccator
12. Oven
13. HDPE bottles with screw cap 60, 125 and 1000 mL (Nalgene[®], USA.)

3.2 Chemicals and Reagents

The chemicals and reagents used for this thesis were listed in Table 3-4.

Table 3-4 The chemicals and reagents used for this thesis

Chemicals and reagents	Grade	Supplier
1. Acetic acid (glacial 100% anhydrous)	Analytical	MERCK, Germany
2. Barium chloride crystals	Analytical	CARLO ERBA
3. Chromium standard solution (1000 mg L ⁻¹)		BDH, England
4. Chromium sulfate basic	Analytical	Fluka-Garantie
5. Ethanol	Absolute for analysis	MERCK, Germany
6. Hydrochloric acid fuming 37%	Analytical	MERCK, Germany
7. Iron standard solution (1000 mg L ⁻¹)		MERCK, Germany
8. Iron (II) sulphate.7H ₂ O	Analytical	Ajax Finechem
9. Magnesium chloride anhydrous	Analytical	MERCK, Germany
10. Nickel standard solution (1000 mg L ⁻¹)		BDH, England
11. Nickel sulphate.6H ₂ O	Laboratory reagent	Asia Pasific Specialty
12. Nitric acid 65%	Analytical	MERCK, Germany
13. Phenolphthalein	Laboratory chemicals	MAY & BAKER, England
14. Potassium biphthalate crystals	Acidimetric standard	J.T. Baker [®] , USA
15. Potassium nitrate	Analytical	BDH, England
16. Sodium acetate anhydrous	Analytical	MERCK, Germany
17. Sodium hydroxide anhydrous pellets	Analytical	CARLO ERBA
18. Sodium sulphate anhydrous	Analytical	CARLO ERBA
19. Sulfuric acid	Analytical	J.T. Baker [®] , USA

3.3 Preparation of solutions

1. Hydrochloric acid solution 5% v/v

Hydrochloric acid (HCl) solution was prepared by direct dilution from the concentrated hydrochloric acid solution with deionized (DI) water. It was used for cleaning of cation exchange membrane (CEM), anion exchange membrane (AEM) and spacer in electro dialysis stack.

2. Nitric acid solution 1% v/v

Nitric acid (HNO₃) solution was prepared by direct dilution from the concentrated nitric acid solution with deionized (DI) water.

3. Sulfuric acid solution 0.04 N

Sulfuric acid (H₂SO₄) solution was prepared by direct dilution from the concentrated sulfuric acid solution with deionized (DI) water.

4. Buffer solution

Buffer solution was prepared by dissolving about 14 g of magnesium chloride anhydrous (MgCl₂), about 3 g of sodium acetate anhydrous (CH₃COONa) and about 1 g of potassium chloride (KNO₃) in 20 mL of acetic acid (CH₃COOH) and 500 mL of deionized (DI) water was added and diluted to 1 L in a volumetric flask.

5. Stock standard sulfate solution 100 mg L⁻¹

A 0.1479 g of sodium sulfate anhydrous (Na₂SO₄) was dissolved in deionized (DI) water and diluted to 1 L in a volumetric flask.

6. Potassium biphthalate solution 0.05 N

Potassium biphthalate (KHC₈H₄O₄) was dried in an oven at 120 °C for 2 hours and cooled in a desiccator before use. A 10 g of KHC₈H₄O₄ was dissolved in deionized (DI) water and diluted to 1 L in a volumetric flask. The exact concentration was calculated.

7. Sodium hydroxide solution 0.1 N

A 4 g of sodium hydroxide (NaOH) was dissolved in deionized (DI) water and diluted to 1 L in a volumetric flask.

8. Electrolyte solution 0.50 N

About 35.5 g sodium sulphate anhydrous (Na_2SO_4) was dissolved in deionized (DI) water and diluted to 1 L in a volumetric flask. It was used for both electrolyte tank (the catholyte and the anolyte tanks).

9. Indicator phenolphthalein solution

About 5 g of phenolphthalein was dissolved in 500 mL of ethanol ($\text{C}_2\text{H}_5\text{OH}$) and diluted to 1 L in a volumetric flask.

10. Working standard chromium solution 100 mg L^{-1}

A 10 mL of the stock standard chromium solution (1000 mg L^{-1}) was pipette and diluted with nitric acid solution (1% v/v) in a 100 mL volumetric flask.

11. Working standard iron solution 500 mg L^{-1}

A 50 mL of the stock standard iron solution (1000 mg L^{-1}) was pipette and diluted with nitric acid solution (1% v/v) in a 100 mL volumetric flask.

12. Working standard nickel solution 100 mg L^{-1}

A 10 mL of the stock standard iron solution (1000 mg L^{-1}) was pipette and diluted with nitric acid solution (1% v/v) in a 100 mL volumetric flask.

13. Real wastewater sample

Real wastewater sample was taken from the pickling process at the Stainless Steel Home Equipment Manufacturing Co., Ltd. The wastewater sample was collected in a 20 L polyethylene (PE) tank.

14. Synthetic sulfuric waste solution

Synthetic sulfuric waste solution was prepared according to the concentration of metal ions, and acid content determined in the real wastewater sample. Synthetic sulfuric waste solutions containing only iron in 0.04 N and 0.10 N sulfuric acid were prepared by dissolving an appropriate amount of iron (II) sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in sulfuric acid. Synthetic sulfuric waste solution containing iron, chromium, and nickel was prepared in 0.04 N sulfuric acid by dissolving appropriate amounts of iron (II) sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) and chromium sulfate basic ($\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$) in sulfuric acid.

3.4 Analytical methods

3.4.1 Acid concentration

The acid concentration was determined by titration method with standard Sodium hydroxide solution. Sodium hydroxide was first standardized with Potassium biphthalate solution. The concentration of sodium hydroxide was calculated as shown below.

$$C_{\text{NaOH}} = C_{\text{KHP}} \times V_{\text{KHP}} / V_{\text{NaOH}}$$

where:

C_{KHP} = exact concentration of KHP (mol L^{-1})

V_{KHP} = volume of KHP solution (mL)

V_{NaOH} = volume of NaOH solution (mL)

The acid concentration in the sample was determined by titration with known concentration of sodium hydroxide and calculated as shown below.

$$C_{\text{acid}} = C_{\text{NaOH}} \times V_{\text{NaOH}} / V_{\text{pipetted sample}}$$

where:

C_{acid} = concentration of acid in the sample (N)

C_{NaOH} = concentration of sodium hydroxide (N)

V_{NaOH} = volume of sodium hydroxide solution (mL)

$V_{\text{pipetted sample}}$ = volume of pipette sample (mL)

3.4.2 Heavy metals

Flame atomic absorption spectrometer (FAAS) was used for determination of the concentration of heavy metals ions in the sample.

1. Preparation of calibration curve

1.1 Standard chromium solutions of 0.5 - 2.5 mg L⁻¹ were used for calibration from the working standard chromium solution and adjusted with nitric acid solution. The absorbance of chromium ions was measured at 357.9 nm.

1.2 Standard iron solutions of 50 – 300 mg L⁻¹ were used for calibration from the working standard iron solution and adjusted with nitric acid solution. The absorbance of iron ions was measured at 305.9 nm.

1.3 Standard nickel solutions of 2 – 10 mg L⁻¹ were used for calibration from the working standard nickel solution and adjusted with nitric acid solution. The absorbance of nickel ions was measured at 232.0 nm.

2. Calibration curve was plotted between the absorbance and the concentration and used for determination of heavy metals ion in a sample.

3.4.3 Sulfate (SO₄²⁻)

Sulfate ions (SO₄²⁻) was determined by turbidity method. First sulfate ion was precipitated with barium chloride (BaCl₂) in an acetic acid medium to form uniform size barium sulfate (BaSO₄) crystals. Light absorbance of the BaSO₄ suspension was measured by UV-Vis spectrophotometer and the concentration of sulfate ions (SO₄²⁻) was determined by using calibration curve.

1. Preparation of calibration curve

Standard sulfate solutions at 5 – 30 mg L⁻¹ were prepared by pipetting stock standard sulfate solution and adjusted with deionized (DI). Blank solution was deionized (DI) water.

2. Sample was prepared by pipetting from sample solution and adjusted with deionized (DI) water.

3. Formation of barium sulfate turbidity

Buffer solution was added and stirred in each concentration of standard sulfate solution and the sample solution. After, spoonful of barium chloride crystals (BaCl_2) was added and stirred at constant speed for 60 ± 2 s. BaCl_2 was not added in the blank solution.

4. Measurement of barium sulfate turbidity

The absorbance of sulfate ion was measured at 420.0 nm. The calibration curve was plotted between the absorbance and the sulfate concentration.

3.5 The removal of heavy metals ions by the electro dialysis process

In all experiments, the synthetic sulfuric waste solution was used for the diluate tank. Sulfuric acid solution (0.04 N) was used for the concentrate tank. Sodium sulphate solution (0.50 N) was used as electrolyte solution for the both electrodes (cathode and anode). The metal concentrations, acid concentration, pH, and sulfate concentration in the sample were determined prior to treatment and after treatment for every 30 minutes for 5 hours. The current of the system was also monitored for determination of current efficiency and specific power consumption.

3.5.1 Batch mode operation

A diagram of the batch mode electro dialysis process, which was used for study of the effect of operational parameter in the removal of heavy metals ions, was shown in Figure 3-2.

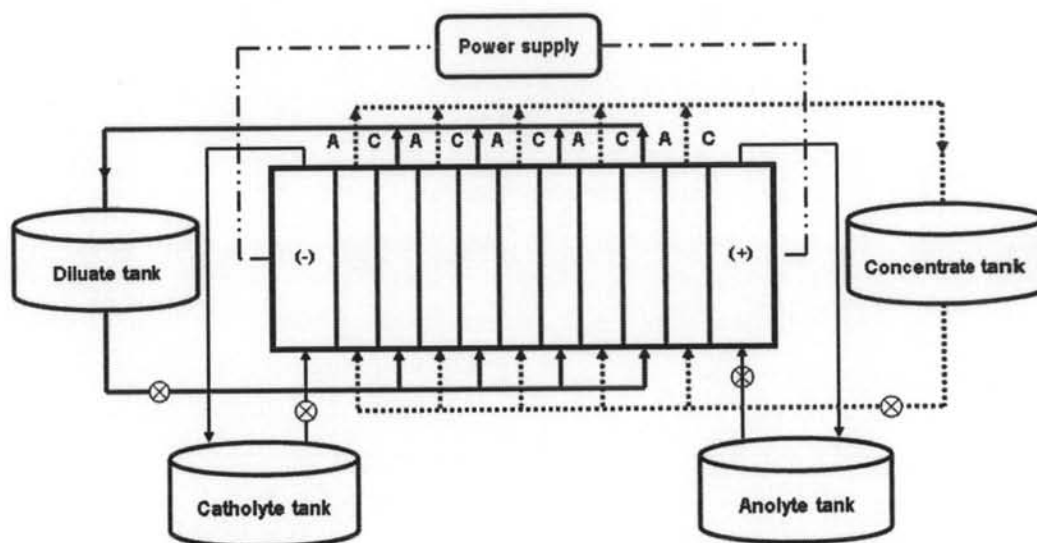


Figure 3-2 A diagram of the batch mode electrodiolysis process.

C = Cation exchange membrane (CEM)

A = Anion exchange membrane (AEM)

+ = Anode

- = Cathode

3.5.1.1 Effect of electric potential on the removal of iron ions

Transportation of ion through ion exchange membrane may be affected by applied electric potential. High electric potential was expected to drive more ions through the membrane; however, too high electric potential would consume more energy. In this experiment, the synthetic sulfuric waste solution (0.04 N) containing only iron ion was used and applied electric potentials of 2.5, 5.0 and 7.5 V were studied.

3.5.1.2 Effect of initial acid concentration on the removal of iron ions

Since sulfuric waste samples may contain variety of acid concentrations; the effect of initial acid concentration was studied for removal of iron ion. The synthetic wastewater solution containing iron ion in sulfuric acid solution was used in this experiment. The operation was carried out using different initial acid concentration (0.04 and 0.10 N). The applied potential of 5.0 V was used.

3.5.1.3 Effect of other elements on the removal of iron ions

Since sulfuric waste samples contain other metal ions such as chromium and nickel; the effect of other metal ions was studied for removal of iron ion. The synthetic wastewater solution containing iron, chromium, and nickel ions in sulfuric acid solution (0.04 N) was used in this experiment. The applied potential of 5.0 V was used. The portions of diluate and concentrate solutions were taken from the outlets every 30 minutes for 5 hours for determination of metal concentrations, acid concentration, and sulfate concentration. The current of the system was also monitored.

3.5.2 Evaluation of experimental data

After the wastewater sample was treated by electro dialysis process, the result of experimental data can be calculated in terms of removal (%), current density (i), current efficiency (%) and specific power consumption (SPC).

1. Removal (%) of heavy metal ion was calculated as follow:

$$\text{Removal (\%)} = [(C_0 - C) / C_0] \times 100$$

where:

C_0 = initial concentration of diluate tank solution (mg L^{-1})

C = concentration of diluate tank solution during time interval
(mg L^{-1})

2. Current density (i) was the driving force of the process since it determines the quantity of equivalent grams transported across the membranes. It was determined using a general definition by assumption of constant concentration in the cell compartment as follow:

$$i = dl / dA_m = I / A_m$$

where:

I = current (A) which I can be measured in each run

A_m = active membrane area (cm^2)

i = current density (A cm^{-2})

3. Current efficiency (η) was measured as the ratio of chemical equivalents of ions effectively migrated from the solutions to the number of electrical equivalents used in the removal process through a membrane pair [46]:

$$\eta = \frac{\text{No. of chemical equivalents effectively migrated}}{\text{No. of electrical equivalents used in ED process}}$$

Current efficiency was calculated according to:

$$\eta = z F V_D \Delta C / N \int_0^t I(t) dt$$

where:

η = current efficiency

z = charge of the ion

F = Faraday constant ($96,500 \text{ A s mol}^{-1}$)

V_D = diluate stream volume (L)

ΔC = inlet concentration in diluate tank – outlet concentration in diluate tank (mol L^{-1})

N = number of cell pairs

I = current (A) and t = time (s)

4. Specific power consumption (EC or SPC) was calculate from

$$\text{SPC} = [E \int_0^t I(t) dt] / V_D$$

where:

E = Applied stack potential (V)

I = Current (A)

SPC = Specific power consumption (kW h m⁻³)

V_D = dilute stream volume (m³)

t = time (s)

3.6 Electrodialysis process for removal of metal ions from the real sulfuric wastewater sample

The wastewater sample was taken from the pickling baths, where the sulfuric acid was used for the removal of rust on metal surface, the Stainless Steel Home Equipment Manufacturing Co., Ltd. Once sample was used in the study. After, the brown suspension was generated in the wastewater sample. Thus, the wastewater sample was digested with nitric acid before the experiment.

The metal concentrations, acid concentration, pH and sulfate concentration in the sample were determined prior to treatment and after treatment for every 30 minutes for 5 hours. The current of system was also monitored for determination of current efficiency and specific power consumption.