

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Analysis of components in real sulfuric wastewater sample

The sulfuric wastewater sample was taken from the pickling bath in the Stainless Steel Home Equipment Manufacturing Co., Ltd. The concentration and composition of the sulfuric wastewater sample were analyzed in order to obtain the initial values of heavy metals ions and prepare the synthetic sulfuric wastewater for this study. The compositions in the wastewater sample were listed in Table 4-1.

**Table 4-1** Parameters of the several compositions in the wastewater sample.

Parameters	Values	Standard Values
Total iron ( $\text{mg L}^{-1}$ )	295.10	max. $10 \text{ mg L}^{-1}$
Chromium ( $\text{mg L}^{-1}$ )	0.707	max. $0.5 \text{ mg L}^{-1}$
Nickel ( $\text{mg L}^{-1}$ )	0.658	max. $0.2 \text{ mg L}^{-1}$
Concentration of acid (N)	0.040	
pH	1.40	5 to 9
Sulfate ( $\text{g L}^{-1}$ )	1.178	-

The experimental results showed that the concentrations of total iron ions and other heavy metal ions (Ni and Cr) in the wastewater sample were higher than those allowed by the industrial effluent standard regulated by Department of Environmental Quality Promotion [17]. Due to a large amount of sulfuric acid used in this process, it generated highly acidic waste containing high concentration of heavy metals which could cause serious environmental problems. Thus, a wastewater treatment process for removal of heavy metals was necessary before releasing to the environment. Furthermore, it would be better if the wastewater treatment process could provide the

treated waste to be reused or recycled in the metal surface treatment process so that the production cost could be reduced.

## 4.2 The removal of heavy metal ions by the electro dialysis process

### 4.2.1 Preliminary study

The electro dialysis (ED) process was employed in batch mode. Iron ion was the main target for removal study because of its high concentration in the waste sample. Parameters such as the effect of electric potential, the effect of initial acid concentration and the effect of other elements were studied for removal of iron ion in the synthetic sulfuric wastewater sample. The synthetic sulfuric wastewater sample containing iron concentration as determined from the real sulfuric wastewater sample (Table 4-1) was used for this study. The Electro dialysis Cell Unit (PCCell GmbH model: PCCell ED 64-4) was used and the initial setup of the electro dialysis stack was shown in Figure 2-5.

The membrane stack consisted of 5 cell pairs where the cation exchange membranes (CEM) were placed at both ends of the stack, near the electrodes (cathode and anode). The synthetic sulfuric wastewater sample was pumped into the ED system through the diluate compartment and the sulfuric acid (0.04 N) was pumped through the concentrate compartment of the system. It was shown in Figure 4-1.

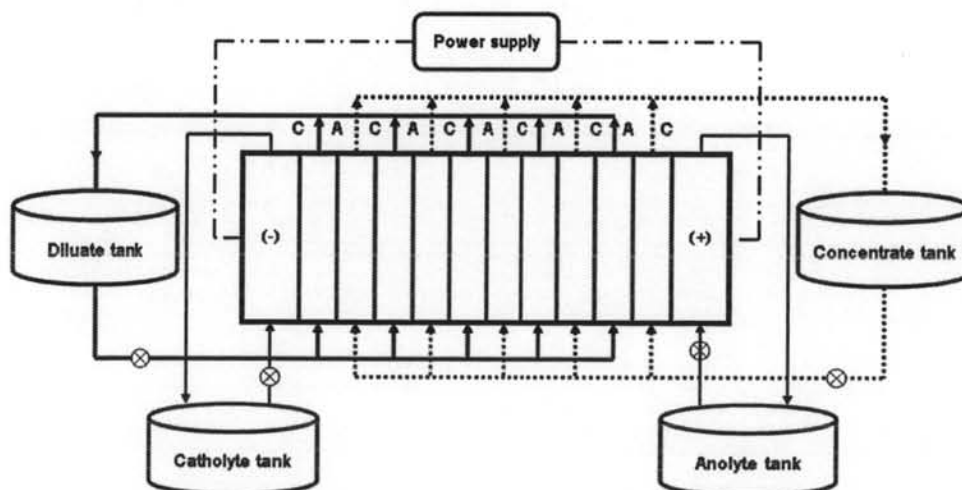
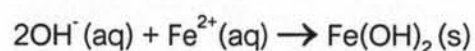
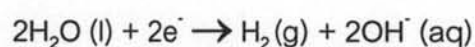


Figure 4-1 A diagram of the initial set up of batch mode electro dialysis process.

First the applied electric potential of 2.5 and 5.0 V were tested. It was observed that the catholyte solution was changed from colorless solution into a solution containing brown suspension when the electric potential of 5.0 V was applied. The brown suspension could be the iron hydroxide precipitate where the iron ions from the diluate compartment could migrate past through the cation exchange membrane toward the cathode and reacted with the hydroxide ions generated from the reduction of water at the cathode.

The reactions were given below.



The migration of ionic species in the initial setup of the electro dialysis cell unit was shown in Figure 4-2.

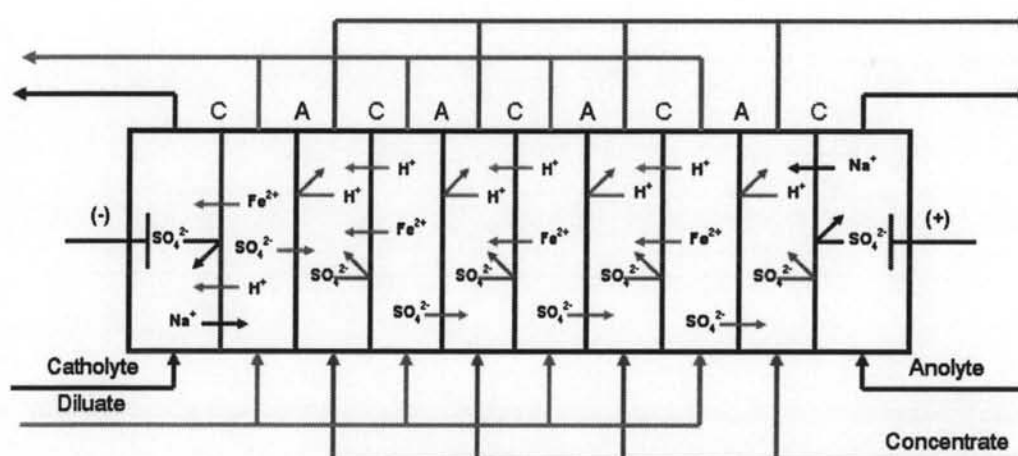


Figure 4-2 The migration of ionic species in the initial setup of the electro dialysis cell unit.

For this reason, the cation exchange membrane (CEM) and spacer nearby the cathode was taken off from the electro dialysis stack (Figure 3-2) and was used throughout this study. The migration of ionic species in the electro dialysis cell unit was shown in Figure 4-3.

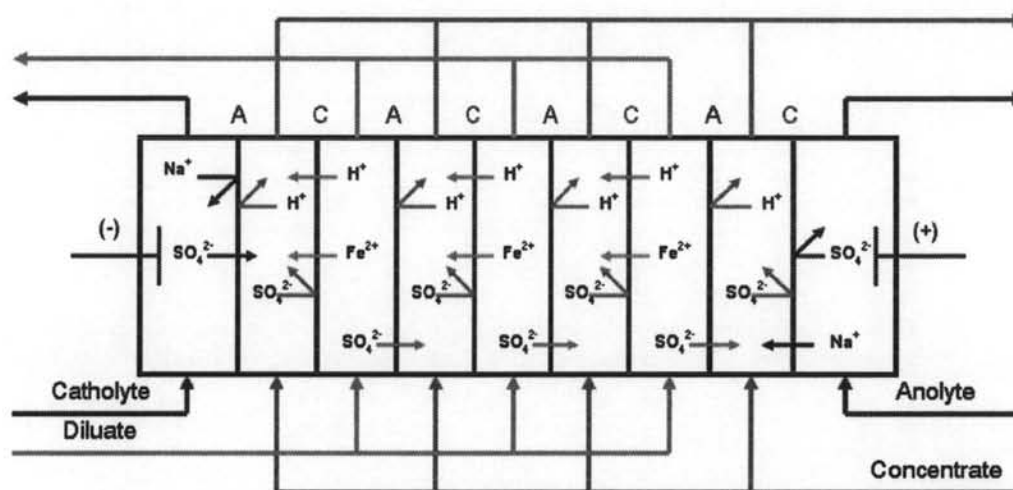
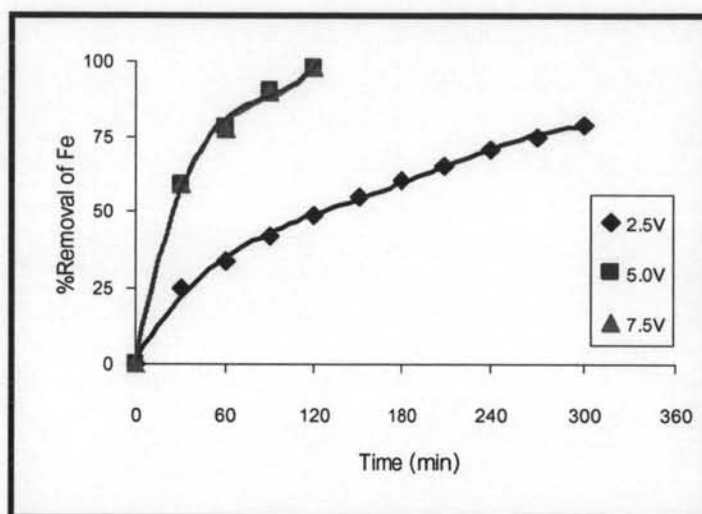


Figure 4-3 The migration of ionic species in the electro dialysis cell unit (after cation exchange membrane and spacer nearby the cathode was taken off).

#### 4.2.2 Effect of electric potential on the removal of iron ion by the ED process

The driving force for transportation of ions through ion exchange membrane in the electro dialysis process was influenced by the applied electric potential. The various applied electric potentials were studied for the removal of iron ions from the synthetic sulfuric wastewater sample. The optimum electric potential was the one that was able to remove most iron ions for a short period of time and consume less energy. The electric potentials of 2.5, 5.0 and 7.5 V were investigated.

The experimental result for the effect of electric potential on the removal (%) of iron ion with time was shown in Figure 4-4.



**Figure 4-4** Effect of electric potential on the removal (%) of iron ion with time (Initial iron ions concentration was about  $295 \text{ mg L}^{-1}$  which dissolved in  $0.04 \text{ N}$  sulfuric acid).

Figure 4-4 showed that the higher electric potential the faster iron ion could be removed. As increased electric potentials, the higher current or current density was observed (Figure 4-5) indicating that the more charges or ions could be transported within the ED system [40]. In the other word, the more iron ion could be transported through the cation exchange membrane from the diluate compartment to the concentrate compartment leading to the complete removal of iron ion in shorter period of time.

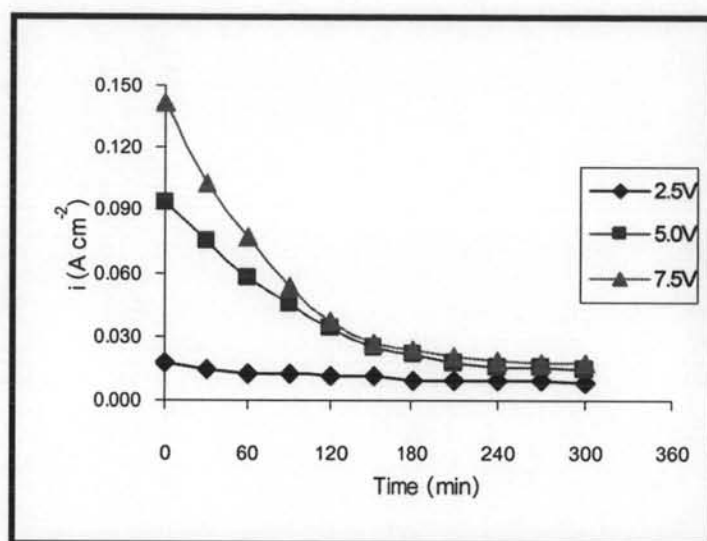
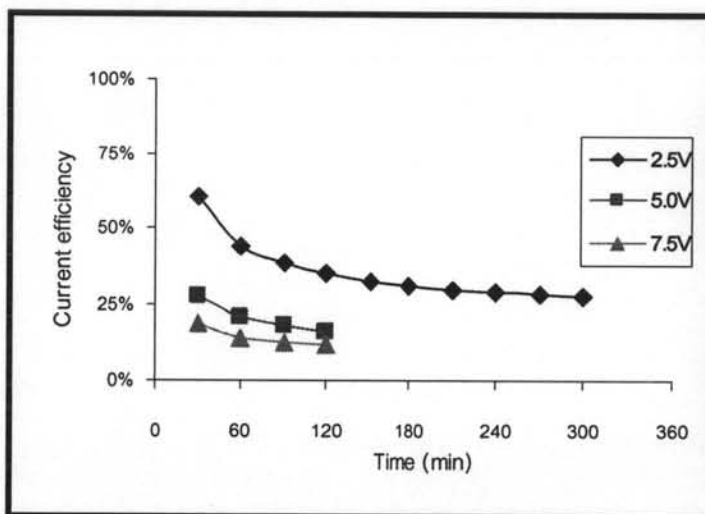


Figure 4-5 The current density ( $i$ ) with time at various applied electric potentials.

Figure 4-5 showed that the initial current density was higher at the higher electric potential. After the time was increased, the current density was rapidly decreased because of the transportation of ions through the membrane from the diluate compartment to the concentration compartment.

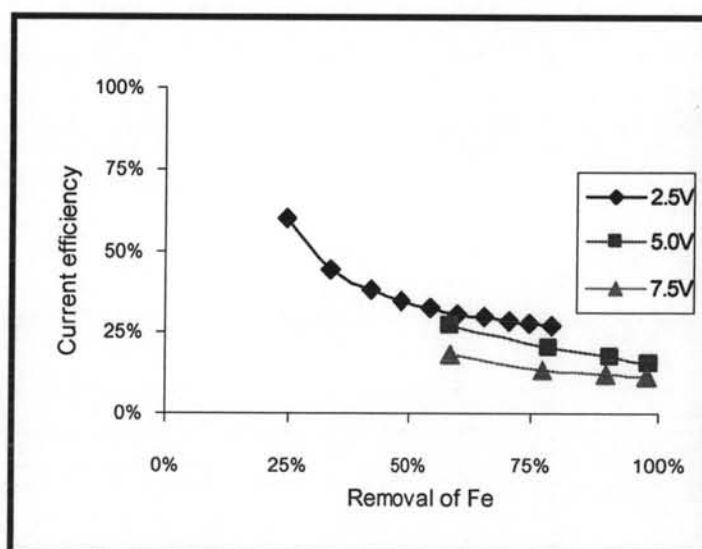
It was also observed in Figure 4-4 that the iron removal (%) time profiles at applied electric potential of 5.0 and 7.5 V were almost identical. Since the flow rate of each batch mode operation in this experiment was not controlled; the iron removal (%) time profiles for 2.5 and 7.5 V were operated at  $16 \text{ L hr}^{-1}$  but for 5.0 V was operated at  $20 \text{ L hr}^{-1}$ , it might have affected the removal of iron ion. According to the Nernst idealization, the higher the flow rate, the less the thickness of the boundary layer adjacent to the membrane surface [45]. As a result, the ions could migrate faster through the smaller boundary layer thickness. Thus, for the study of iron removal at 5.0 V operated at  $20 \text{ L hr}^{-1}$ , the iron ions could be transported into the membrane faster than that they were supposed to if operated at  $16 \text{ L hr}^{-1}$ . That might be the reason why the iron removal time profile at 5.0 V was similar to that at 7.5 V. Therefore, it was important to use the highest practicable flow rates in order to have the lowest thickness of the boundary layer and to have uniform velocities at all points along the membranes surface [47].

The current efficiency for removal of iron ion profile for removal of iron ion at various applied electric potentials was displayed in Figure 4-6.



**Figure 4-6** The current efficiency for removal of iron ion with time at various applied electric potentials.

The experimental result for the effect of electric potential on the current efficiency with the removal of iron ion was shown in Figure 4-7.



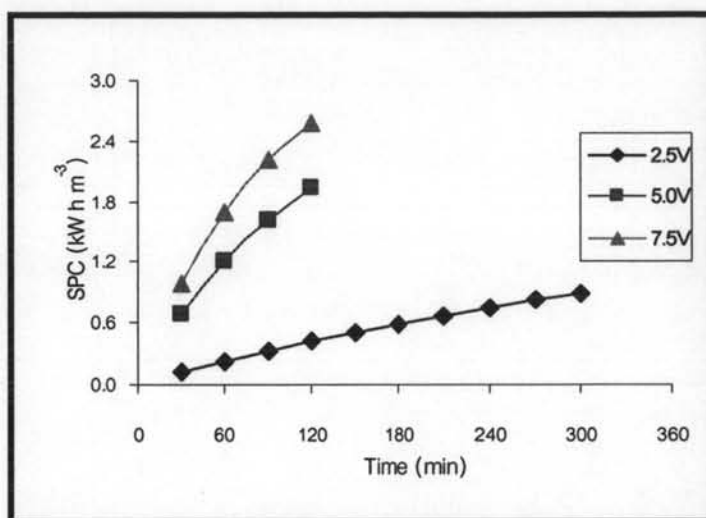
**Figure 4-7** The current efficiency for removal of iron ion with the removal of iron ion at various applied electric potentials.

Considering the experimental results in Figure 4-6 and Figure 4-7, it was found that at high electric potential, the current efficiency for removal of iron ion was lower than at low electric potential. At low electric potential, the total current was low and mostly attributed to the transportation of iron ions, thus the term  $\Delta C/I$  was high. At high electric potential, the total current was high, and shared by the transportation of other ions due to depletion of iron ion, thus the term  $\Delta C/I$  was low. Furthermore, despite the fact that the overall current efficiency (%) at 2.5 V was higher than that at 5.0 and 7.5 V but the period for the removal of iron ion was much longer. Since the iron removal times at 5.0 and 7.5 V were not much different but the current efficiency for removal of iron ion at 5.0 V was higher than that at 7.5 V, electric potential of 5.0 V was selected for using in the next experiment.

For the electro dialysis (ED) stack, the cost related to energy consumption was a strong function of the operating parameter such as current density ( $i$ ), electric potential drop across the electro dialysis (ED) stack and operating time. From the economical viewpoint, the effects of working parameter on energy consumption (EC) were studied. Specific power consumption (SPC) was calculated from equation in the chapter III [40].

The experimental result for the effect of electric potential on the specific power consumption (SPC) with time was shown in Figure 4-8.





**Figure 4-8** The specific power consumption (SPC) with time at various applied electric potentials.

Figure 4-8 showed that the specific power consumption (SPC) was remarkably affected by the changes in applied electric potential. It was obtained that the specific power consumption (SPC) was increased when a higher voltage was applied. SPC value was risen from 0.43, 1.94 and 2.89  $\text{kW h m}^{-3}$  when the applied electric potential increased from 2.5, 5.0 and 7.5 V within 2 hours.

Furthermore, the concentration of acid and sulfate in the diluate tank were decreased because cation ( $\text{H}^+$ ) and anion ( $\text{SO}_4^{2-}$ ) could also migrate through the cation exchange membrane (CEM) and anion exchange membrane (AEM), respectively. The changes of pH of acid and concentration of sulfate in the diluate tank were shown in Figure 4-9 and Figure 4-10, respectively.

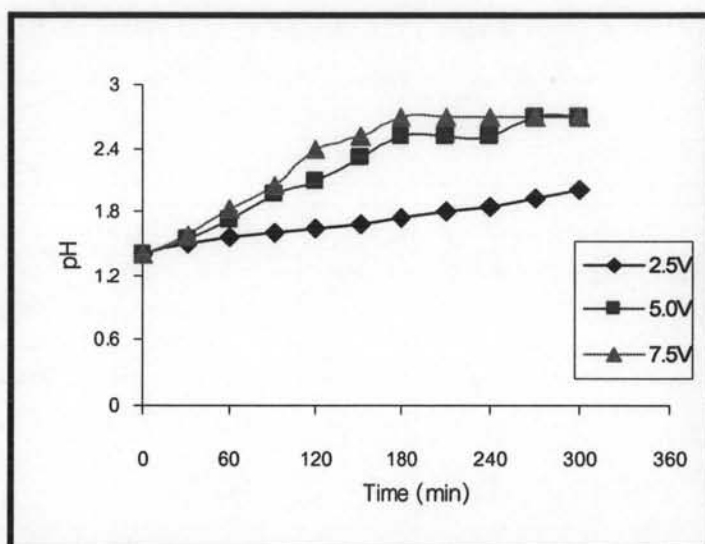


Figure 4-9 The pH of acid with time at various applied electric potentials.

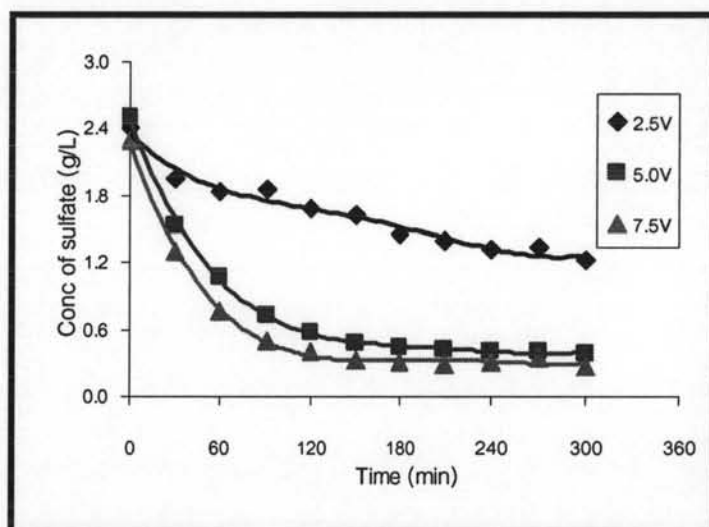


Figure 4-10 The concentration of sulfate with time at various applied electric potentials.

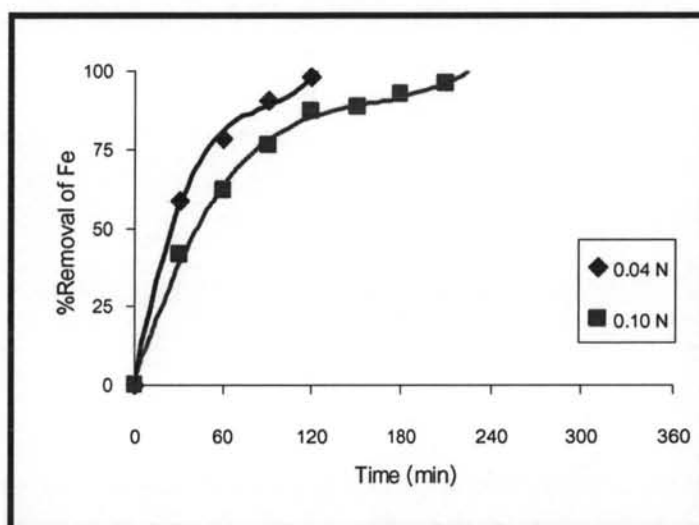
Considering the experimental results in Figure 4-4 with Figure 4-9, it was found that the iron ions could be removed about 98% within 2 hours which the pH was about 2.00. The pH was lower than the allowed by industrial effluent standard which can be not released to the environment but it may be reused or recycled as makeup feed in the metal surface treatment process.

#### 4.2.3 Effect of initial acid concentration on the removal of iron ion by the ED process

The initial acid concentration was studied due to that the surface treatment process of metal industries may use variety of concentrations of acid solution between 0.04 to 0.10 N depending on types of metals or times of the pre-cleaning process and removal of rust process. Thus, the effect of initial acid concentration was investigated at 0.04 and 0.10 N as the electric potential was fixed at 5.0 V.

The flow rate of each batch mode operation in this experiment was not controlled. The iron removal (%) time profiles for 0.04 N and 0.10 N were operated at 20 and 24 L hr<sup>-1</sup>. Since the flow rate was not affected of the removal of iron ion when the electric potential was fixed [47], thus the flow rate was not used for consideration in this experiment.

The experimental result for the effect of initial acid concentration on the removal (%) of iron ion with time was shown in Figure 4-11.

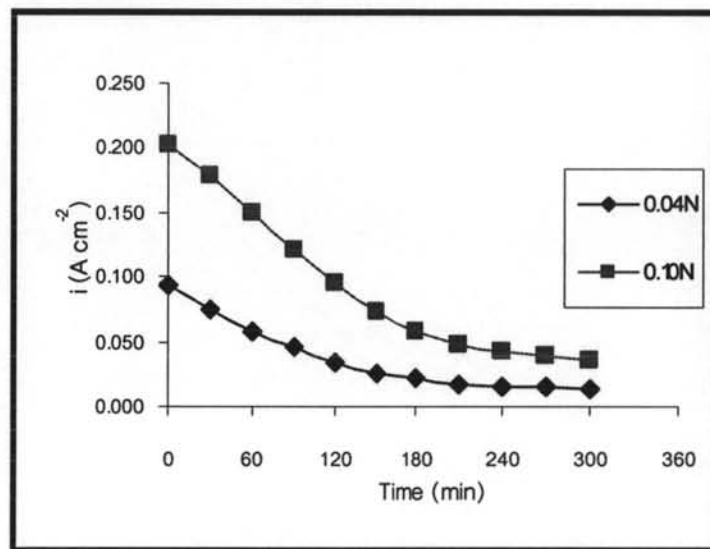


**Figure 4-11** Effect of initial acid concentration on the removal (%) of iron ion with time (Initial iron ion concentration was about 295 mg L<sup>-1</sup> and electric potential at 5.0 V).

Figure 4-11 showed that at high initial acid concentration, the iron ion was removed somewhat slower than at low initial acid concentration. The reason might be that at high initial acid concentration, there were more amounts of hydrogen ions, whose

mobility was relatively faster than that of iron ions, easily transport through the membrane than iron ions resulting to that the transportation of iron ions could be slow down.

In addition, the energy consumption values could be considered. Using high acid concentration increased current density resulting in an increase of energy consumption, shown in Figure 4-12 and Figure 4-13.



**Figure 4-12** The current density ( $i$ ) with time at different initial acid concentrations.

Figure 4-12 showed that at the high initial acid concentration the initial current density was increased due to the increase in the amount of ions in the diluate compartment. After the time was increased, the current density was decreased due to the transportation of ions through the membrane from the diluate compartment to the concentration compartment. Furthermore, at the high initial acid concentration the initial current density was increased because the high conductivity of solution when at equal electric potential (Figure 4-14).

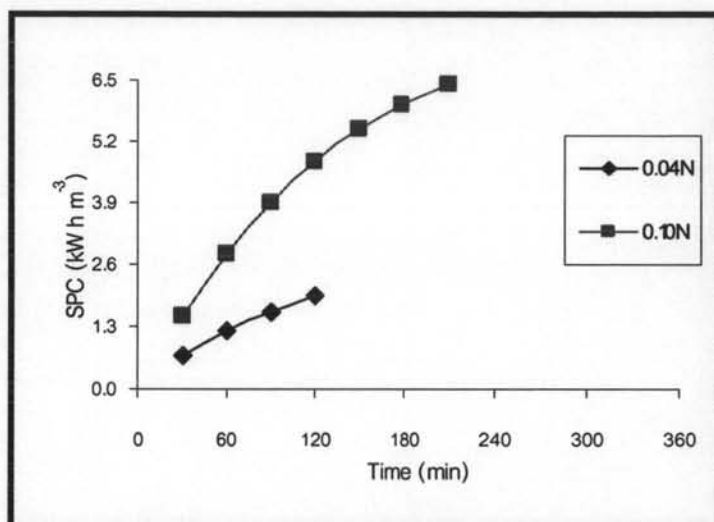


Figure 4-13 The specific power consumption (SPC) with time at different initial acid concentrations.

The specific power consumption (SPC) was remarkably affected by the changes in initial acid concentration. It was obtained that the specification power consumption (SPC) was increased when a higher initial acid concentration was applied. SPC value was increased from 1.94 to 6.49 kW h m<sup>-3</sup> when the initial acid concentration increased from 0.04 and 0.10 N within 2 hours and 3 hours 30 minutes, respectively.

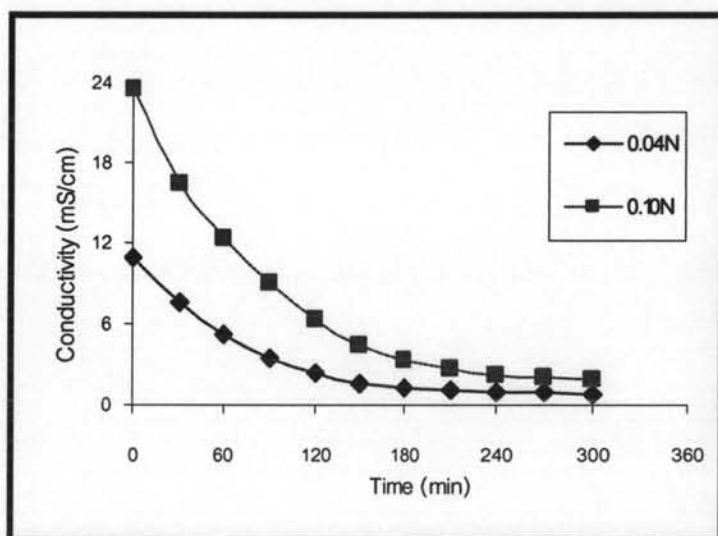
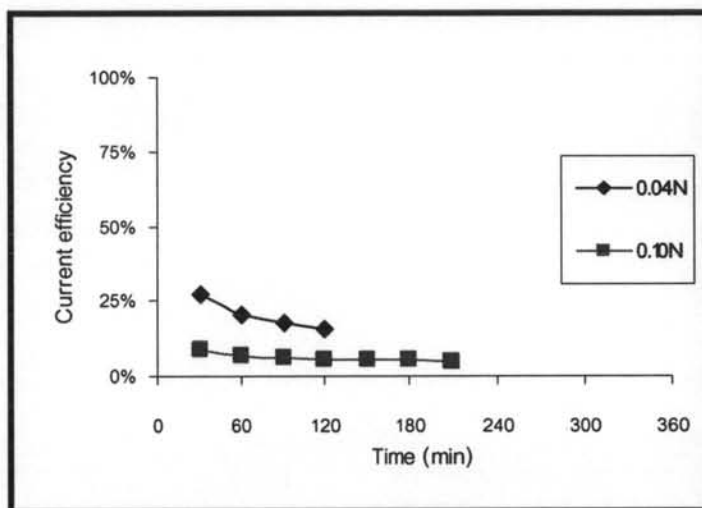


Figure 4-14 The conductivity of solution with time at different initial acid concentrations.

The current efficiency for removal of iron ion profile at various initial acid concentrations was displayed in Figure 4-15



**Figure 4-15** The current efficiency for removal of iron ion with time at different initial acid concentrations.

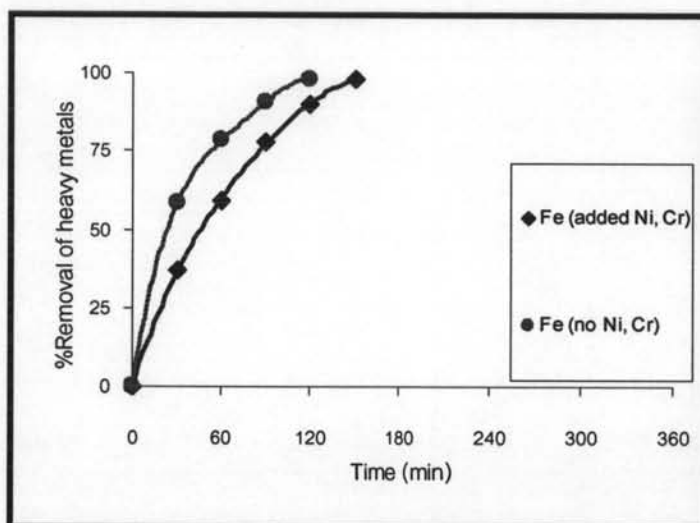
Figure 4-15 showed that at high initial acid concentration the current efficiency for removal of iron ions was lower than at the low initial acid concentration. It probably due to that at high initial acid concentration, the current was mainly a result of transportation of the more amounts of hydrogen ions or proton ( $H^+$ ) that might compete with the iron ions.

#### 4.2.4 Effect of other elements on the removal of iron ion by the ED process

The effect of other elements on the removal of iron ion was used due to that the waste from the surface treatment process of metal industries normally contains other kinds of heavy metals such as Ni and Cr.

The flow rate of each batch mode operation in this experiment was not controlled. The iron removal (%) time profiles for addition of other elements and without addition of other elements were operated at 14 and 20 L hr<sup>-1</sup>. Since, the flow rate was not affected of the removal of iron ion when the electric potential was fixed [48], thus the flow rate was not used for consideration in this experiment.

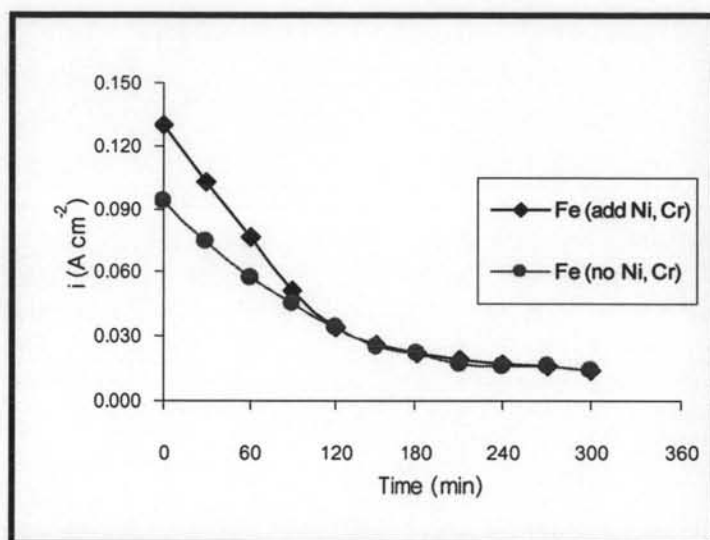
The experimental result for the effect of other elements on the removal (%) of iron ions with time was shown in Figure 4-16.



**Figure 4-16** Effect of other elements on the removal (%) of iron ions with time (Initial iron ion concentration was about  $295 \text{ mg L}^{-1}$  which dissolved in  $0.04 \text{ N}$  sulfuric acid and electric potential at  $5.0 \text{ V}$ ).

Figure 4-16 showed that when other elements (Ni, Cr) were present in the waste solution, the iron ions were slowly removed than when no other elements were added. Because of relatively strong electrostatic interaction between nickel and chromium ions with the active sites of the cation exchange membrane, the transportation of iron ions through the membrane might be inhibited.

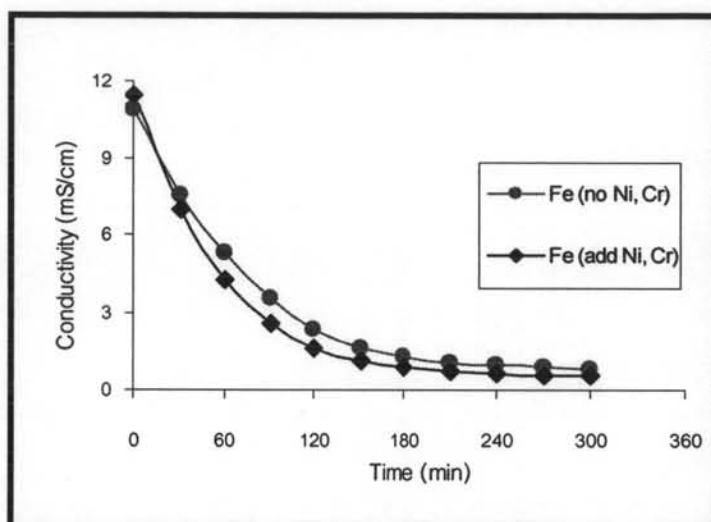
The current density profiles for waste solution with Ni and Cr added and without Ni and Cr added were displayed in Figure 4-17.



**Figure 4-17** The current density ( $i$ ) with time for synthetic waste solution with Ni and Cr added and without Ni and Cr added.

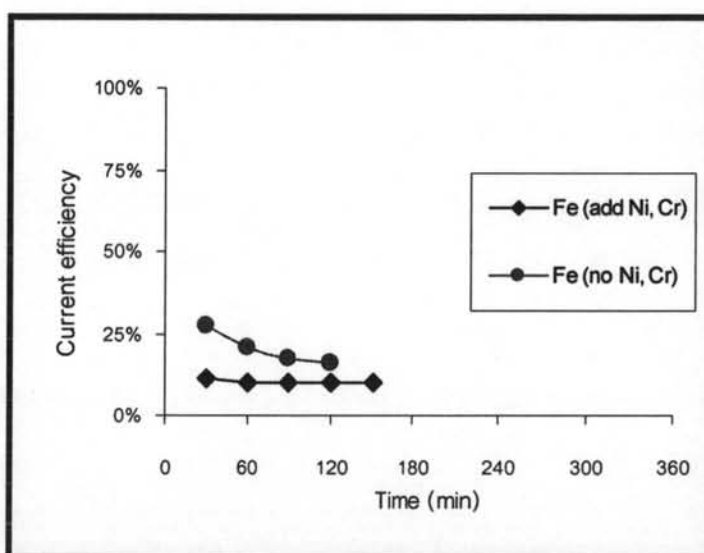
Figure 4-17 showed that the initial current density was higher when other elements (Ni, Cr) were present in the waste solution. After the time was increased, the current density was decreased and was equaled with that when no other elements were added within 2 hours because the conductivity of the solutions between with other elements (Ni, Cr) added and without other elements (Ni, Cr) added was not differed (Figure 4-18). The reason might be that the nickel ions and chromium ions was present in very little amounts in the synthetic sulfuric wastewater sample.





**Figure 4-18** The conductivity of solution with time for synthetic waste solution with Ni and Cr added and without Ni and Cr added.

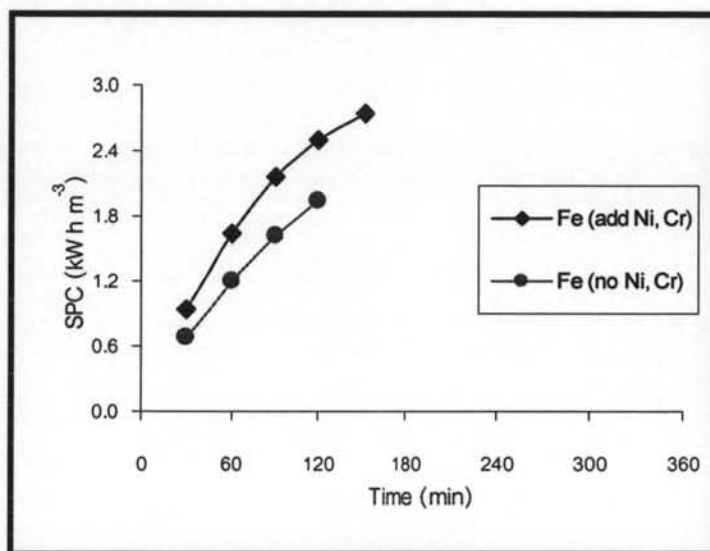
The current efficiency for removal of iron ion profiles for synthetic waste solution with Ni and Cr added and without Ni and Cr added were displayed in the Figure 4-19.



**Figure 4-19** The current efficiency for removal of iron ions with time for synthetic waste solution with Ni and Cr added and without Ni and Cr added

Figure 4-19 showed that when other elements (Ni, Cr) were present in the synthetic waste solution the current efficiency for removal of iron ion was lower than when no other elements were added because the current of ED process was used for the migration of not only iron ion but other ions such nickel, chromium and sulfate ions as well which it was affect with the current efficiency for removal of iron ion.

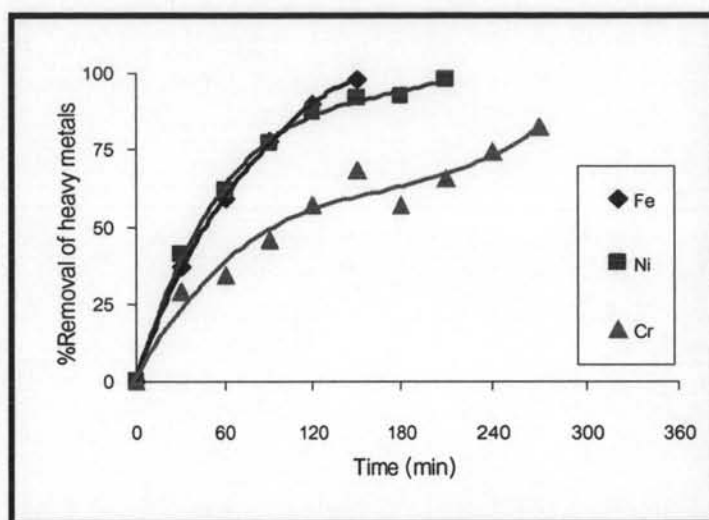
The experiment result for the effect of other elements on the specific power consumption (SPC) with time was shown in Figure 4-20.



**Figure 4-20** The specific power consumption (SPC) with time for synthetic waste solution with Ni and Cr added and without Ni and Cr added

From these results, the specific power consumption (SPC) was remarkably affected by the different of other ion was added in the waste solution. It was obtained that the specific power consumption (SPC) was higher for waste solution with Ni and Cr added. SPC value for complete removal of iron ion was increased from  $1.94 \text{ kW h m}^{-3}$  for waste solution with Ni and Cr added to  $2.75 \text{ kW h m}^{-3}$  for without Ni and Cr added within 2 hours and 2 hours 30 minutes, respectively.

Furthermore, the concentration of nickel and chromium ions in the diluate compartment were decreased due to cation ( $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$ ) could also migrate through the cation exchange membrane (CEM). The removal (%) of heavy metals ions with time was shown in Figure 4-21.



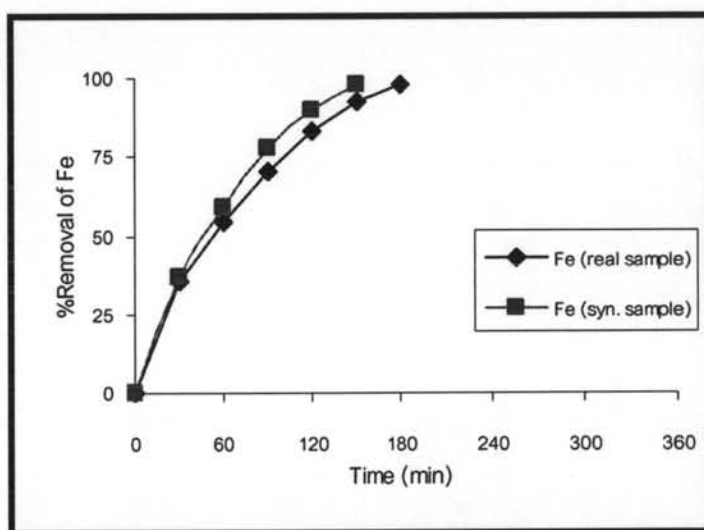
**Figure 4-21** Removal (%) of heavy metal ions with time (Initial iron ion concentration was about  $295 \text{ mg L}^{-1}$ , initial chromium ion concentration was about  $1 \text{ mg L}^{-1}$  and initial nickel ion concentration was about  $1 \text{ mg L}^{-1}$  which dissolved in  $0.04 \text{ N}$  sulfuric acid, electric potential at  $5.0 \text{ V}$  and flow rate at  $14 \text{ L hr}^{-1}$ ).

From these results, the period for the removal of chromium ion was longer than the removal of nickel ion and iron ion because of the effect of electrostatic force between ions with the charge on the ion exchange membranes, which depended on ionic size and oxidation state of ions. The oxidation state of chromium ion was trivalent while the oxidation state of nickel ion and iron ion were divalent. The ionic size of chromium ion ( $\text{Cr}^{3+}$ ) was  $62 \text{ pm}$ , nickel ion ( $\text{Ni}^{2+}$ ) was  $70 \text{ pm}$  and iron ion ( $\text{Fe}^{2+}$ ) was  $77 \text{ pm}$  [48]. Chromium ion was the smallest with the highest charge that could have relatively strong electrostatic interaction with the active site of the cation exchange membrane (CEM). Thus, the transportation of chromium through the membrane would be slowest, while the transportation of nickel and iron were not much different.

### 4.3 Electrodialysis process of the real sulfuric wastewater sample

The electro dialysis process of the real sulfuric wastewater sample was operated at the batch mode in this experiment. The real sulfuric wastewater sample was first digested with nitric acid due to the formation of precipitate of iron during storage. The flow rate in this experiment was  $18 \text{ L hr}^{-1}$ .

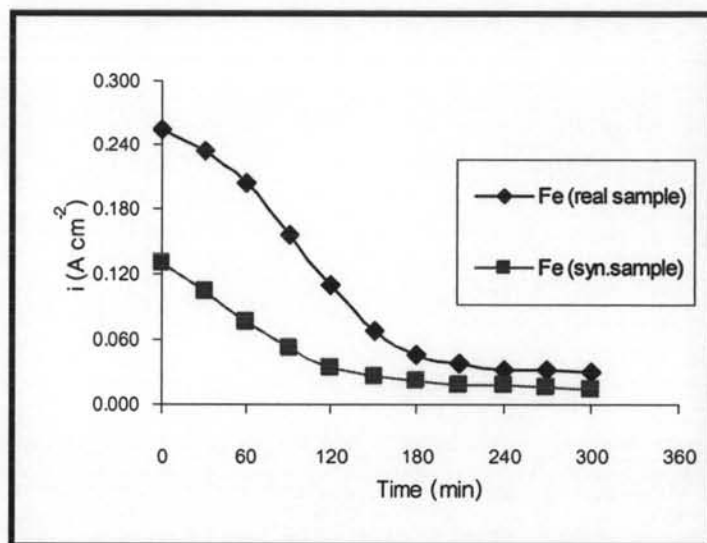
The experimental result for the comparison of the real sulfuric wastewater sample with the synthetic sulfuric wastewater sample on the removal (%) of iron ion with time was shown in Figure 4-22.



**Figure 4-22** Comparison of the real sulfuric wastewater sample with the synthetic sulfuric wastewater sample on the removal (%) of iron ion with time.

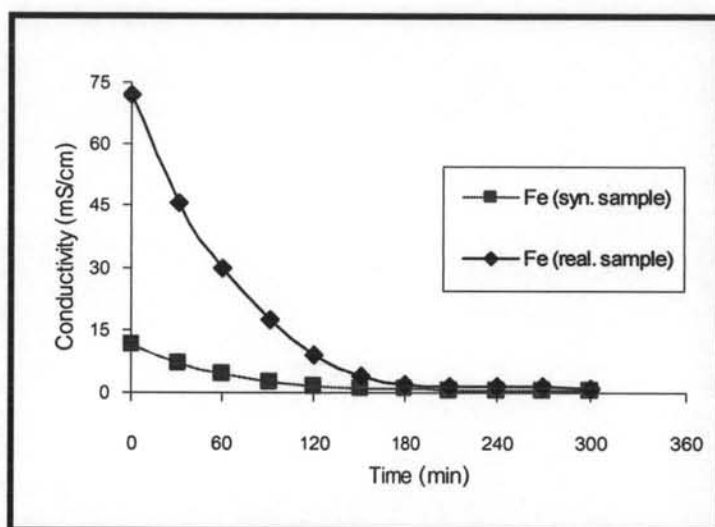
Figure 4-22 showed that the period for the removal (%) of iron ion from the real sulfuric waste sample was not much differed from the synthetic sulfuric sample even though there were large amount of nitric acid used for digestion. It was suggested that the large amount of nitric acid did not much affect the transportation of iron ion through cation exchange membrane (CEM) as described in 4.2.3.

The current density profiles at various iron ion conditions were displayed in Figure 4-23.



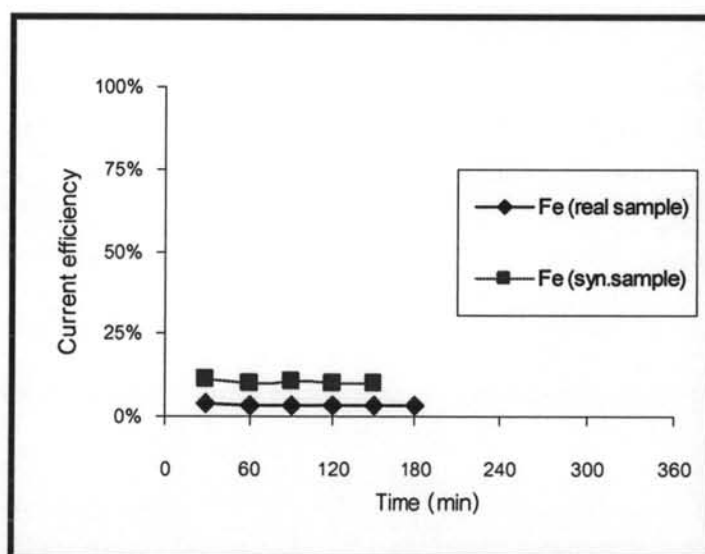
**Figure 4-23** The current density ( $i$ ) with time for the synthetic sulfuric wastewater sample and the real sulfuric wastewater sample.

Figure 4-23 showed that at the real sulfuric wastewater sample the initial current density was higher because the concentration of initial acid was much higher due to the large amount of nitric acid used for digestion. The conductivity of the real sulfuric wastewater sample was higher than the conductivity of the synthetic sulfuric wastewater sample which was shown in Figure 4-24. Nevertheless, after the time was increased, the current density was decreased due to the reason as described in 4.2.3.



**Figure 4-24** The conductivity of solution with time for the synthetic sulfuric wastewater sample and the real sulfuric wastewater sample.

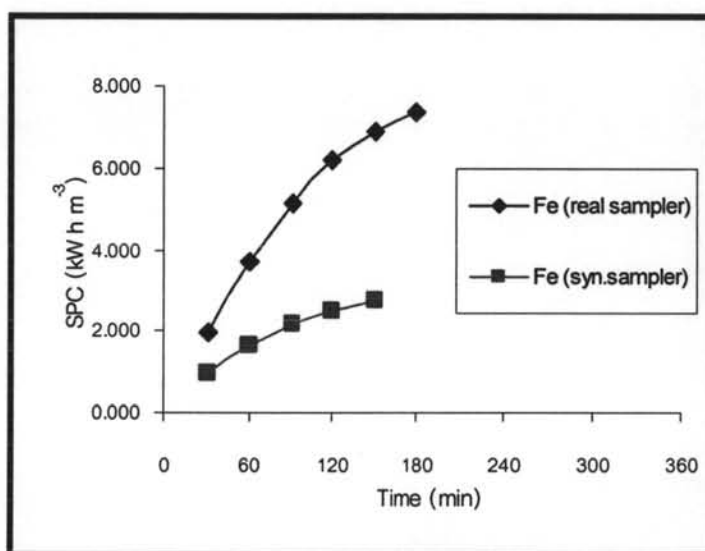
The current efficiency for removal of iron ion profiles for the synthetic sulfuric wastewater sample and the real sulfuric wastewater sample were displayed in Figure 4-25.



**Figure 4-25** The current efficiency for removal of iron ion with time for the synthetic sulfuric wastewater sample and the real sulfuric wastewater sample.

Figure 4-25 showed that the current efficiency for removal of iron ion at the real wastewater sample was lower than at the synthetic sulfuric wastewater because the current of ED process was used for the migration of not only iron ion but other ions such hydrogen, nickel, chromium, sulfate, nitrate and other ions so that the current efficiency for removal of iron ion was decreased.

The experimental result for the comparison of the real sulfuric wastewater sample with the synthetic sulfuric wastewater sample on the specific power consumption (SPC) with time was shown in Figure 4-26.



**Figure 4-26** The specific power consumption (SPC) with time for the synthetic sulfuric wastewater sample and the real sulfuric wastewater sample.

From these result, the specific power consumption (SPC) was remarkably affected by the changes in the synthetic sulfuric wastewater sample and the real sulfuric wastewater sample. It was obtained that the specific power consumption (SPC) was increased when used the real sulfuric wastewater sample. SPC value was increased from 2.75 to 7.38  $\text{kW h m}^{-3}$  when the real sulfuric wastewater sample used in the diluate compartment within 2 hour 30 minutes and 3 hours, respectively.

The composition of sulfuric wastewater sample after treated by electro dialysis process was listed in Table 4-2.

**Table 4-2** Concentration in the wastewater sample before treatment and after treatment by electro dialysis process

Parameters	Before	After	Standard Values
Iron ( $\text{mg L}^{-1}$ )	219.52	4.33	max. 10 $\text{mg L}^{-1}$
Chromium ( $\text{mg L}^{-1}$ )	0.834	0.09	max. 0.5 $\text{mg L}^{-1}$
Nickel ( $\text{mg L}^{-1}$ )	0.603	0.03	max. 0.2 $\text{mg L}^{-1}$
Concentration of acid (N)	0.200	0.003	-
pH	0.70	2.52	5 to 9
Sulfate ( $\text{g L}^{-1}$ )	1.178	0.210	-

**Note:** electric potential at 5.0 V and flow rate at 18  $\text{L hr}^{-1}$

Considering the experimental results in Table 4-2, it was found that the concentration of metals in solution after treatment by electro dialysis process was lower than that allowed by the industrial effluent standard regulated by Department of Environmental Quality Promotion [17]. But the pH of acid was still lower than that allowed by the industrial effluent standard. Thus it can not be released to the environmental but it may be reused or recycled for the surface treatment process by adding or mixing with the new concentrate acid.