CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 The characteristics of wastewater

Wastewater from metal plating industry was collected and analyzed by an Inductively Coupled Plasma Mass Spectrometer. The wastewater contained 565 mg/L Ni, 243.8 mg/L Fe, 0.310 mg/L Zn, and 0.069 mg/L Cu. The pH was 5.48. The water temperature was 29.3 °C, and the conductivity was 32.2 μs/cm. The results of wastewater analysis are shown in Table 4.1.

Table 4.1 Characteristics of wastewater used in the study

Parameter	**Value**
pH	5.48
Conductivity (μs/cm)	32.2
Temperature (° C)	29.3
Ni (mg/L)	565.0
Fe (mg/L)	243.8
Zn (mg/L)	0.310
Cu (mg/L)	0.069

4.2 Nickel adsorption on hydrous ferric oxide (HFO)

4.2.1 Adsorption isotherm

The adsorption isotherm for nickel adsorption was done by Pratomsrimake, (2000). Relationship between the obtained result is closed to Freundlich isotherm equation particularly in logarithmic form (R^2 = 0.9806) as shown in Figure 4.1. K and n obtained from the experiments were 0.112 and 0.63, respectively. The Freundlich isotherm is expressed as,

$$q = KC^{1/n} \tag{4.1}$$

Where C is the concentration of nickel after adsorption

q is the mass of nickel adsorbed per mass of iron scrap

Freundlich Isotherm in logarithmic form can be written as:

$$\log q = \log K + (1/n) \log C \tag{4.2}$$

$$q = 0.1122C^{1/0.63} \tag{4.3}$$

4.2.2 The adsorption test using wastewater from plating industry

The wastewater collected from metal plating industry was diluted to 6.9 mg/L and used in this experiment. The results are shown in Figure 4.2. The reaction between nickel and iron oxide was rapid in the first 200 minutes and nickel removal was 32 % during this period. After this period adsorption became slow. Approximately 20 % nickel was removed between 200 and 600 minutes. After 600 minutes of reaction, it took another 900 minutes just to remove additional 10 % nickel. The percentage of nickel adsorption can be described by Equation (4.4). Iron oxide can probably remove more than 70 % nickel in wastewater if enough reaction time were given.

$$Y = 14.564 \ln (X) - 45.304 \tag{4.4}$$

$$r^2 = 0.8771$$

where Y is percentage nickel removal and X is time (minutes).

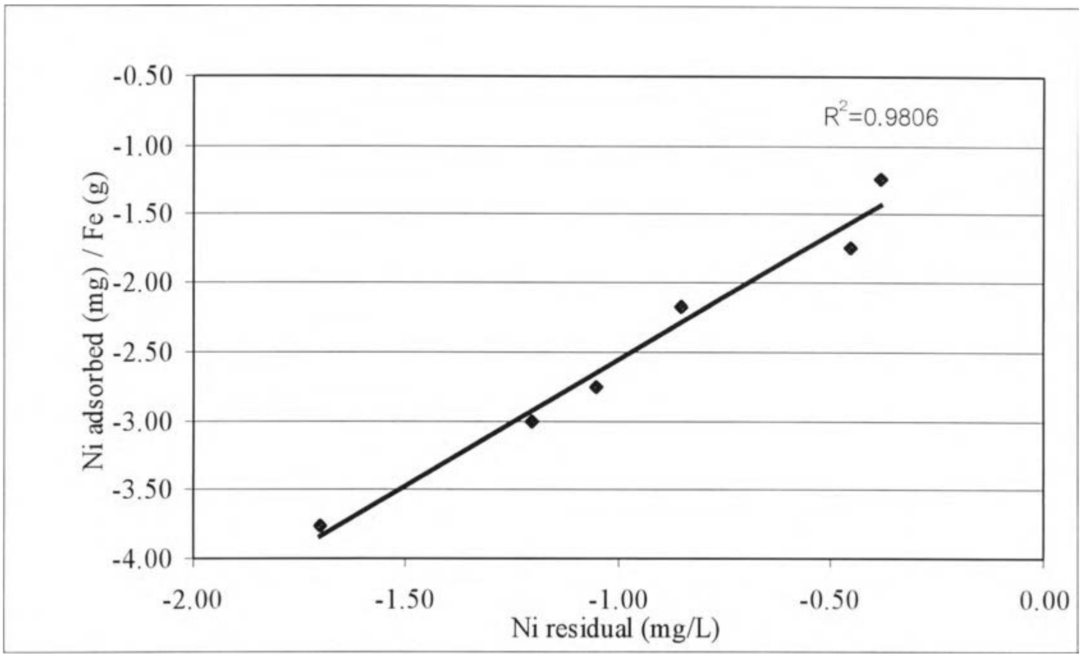

Figure 4.1 Freundlich Isotherm in logarithmic form for nickel adsorbed by iron scrap on 24 hours (Pratomsrimake, 2000).

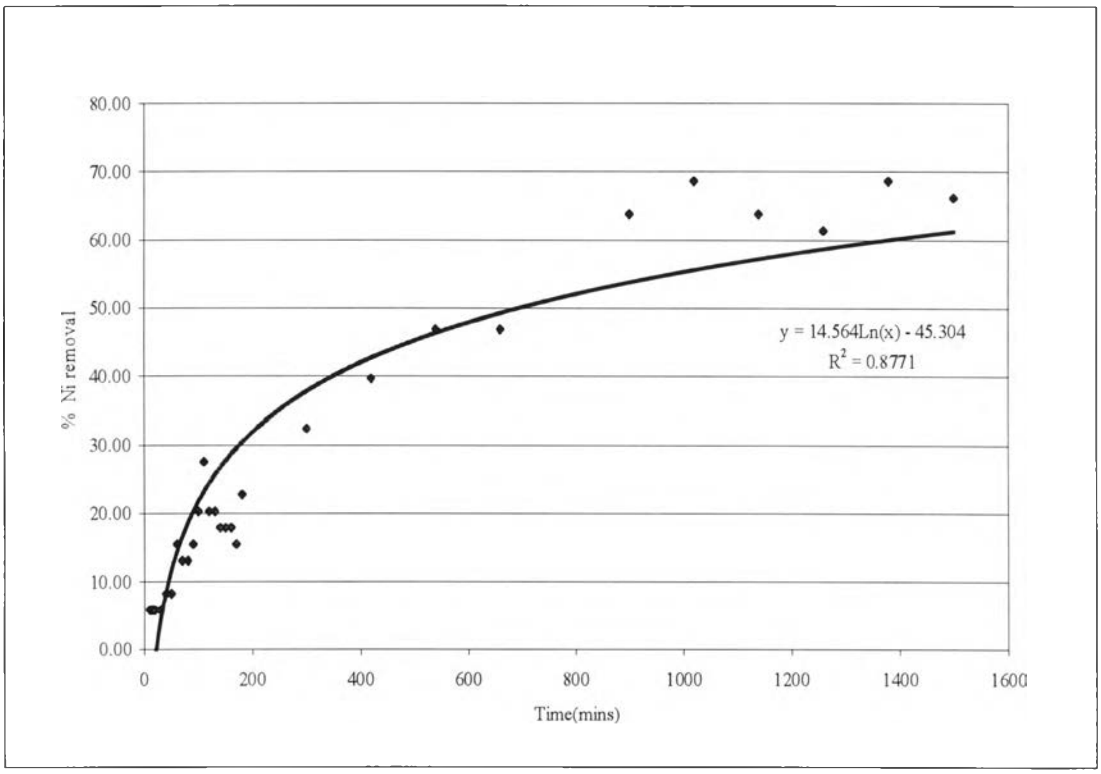

Figure 4.2 Adsorption of nickel with HFO

4.3 Effect of pH on nickel removal percentage

The wastewater was diluted with an influent nickel concentration of 6.9 mg/L and this diluted wastewater was used in this part of the study. The pH was adjusted to the pre-determined value by adding 0.1N HCl or 0.1 N NaOH. The relationship between the amount of nickel sorbed and the initial pH of the test solution is illustrated in Figure 4.3. This figure shows that an increase of pH 5 to 6 caused a decrease in nickel sorption, resulting in lower percentage removal, which was less than 30%. When the pH was raised to above 6, the nickel removal was sharply increased to more than 50%. The nickel removal dropped in the pH range of 7 to 9, and increased in the range of 9 to 10. These phenomena can be explained by the effect of pH on the charge of the iron oxide surface. When the pH increased, the charge and the positive electrostatic potential on the iron oxide surface decreased, resulting in a drop of HFO sorption capacity.

Metals can adsorb to the metal oxide surface according to the following equilibrium (Stumm and Morgan, 1995):

$$\text{S-OH} + M^{2+} = \text{S-OM}^{(2-1)+} + H^{+} \qquad (4.5)$$

S-OH = oxide surfaces

M^{2+} = metal

In basic solution, nickel ions adsorb to the oxide surfaces and proton (H^{+}) is released. In acidic solution, the reactions are reversed (desorption) and nickel ions are released. The relationship between nickel sorption and test pH in the first 200 minutes is shown in Figure 4.4. In this experimental, nickel removal was the highest at pH 7. The relationship between nickel adsorbed in milligram per gram of iron and pH is shown in Figure 4.5. Calculation was conducted to determine the maximum nickel adsorbed per gram of iron. It was found to be approximately 400 mg nickel per gram of iron at pH 7. The results obtained confirm the concept described above. The decrease of nickel removal at low pH was probably caused by the release of nickel ions from surface. Therefore, it is recommended that the removal of nickel with iron oxide the pH be maintained in neutral range. It has been reported that the hydroxyl group was the dominant adsorbable species in the pH range of 6 to 7 for nickel ions adsorded by iron oxide (Jame and Dauglas, 1990).

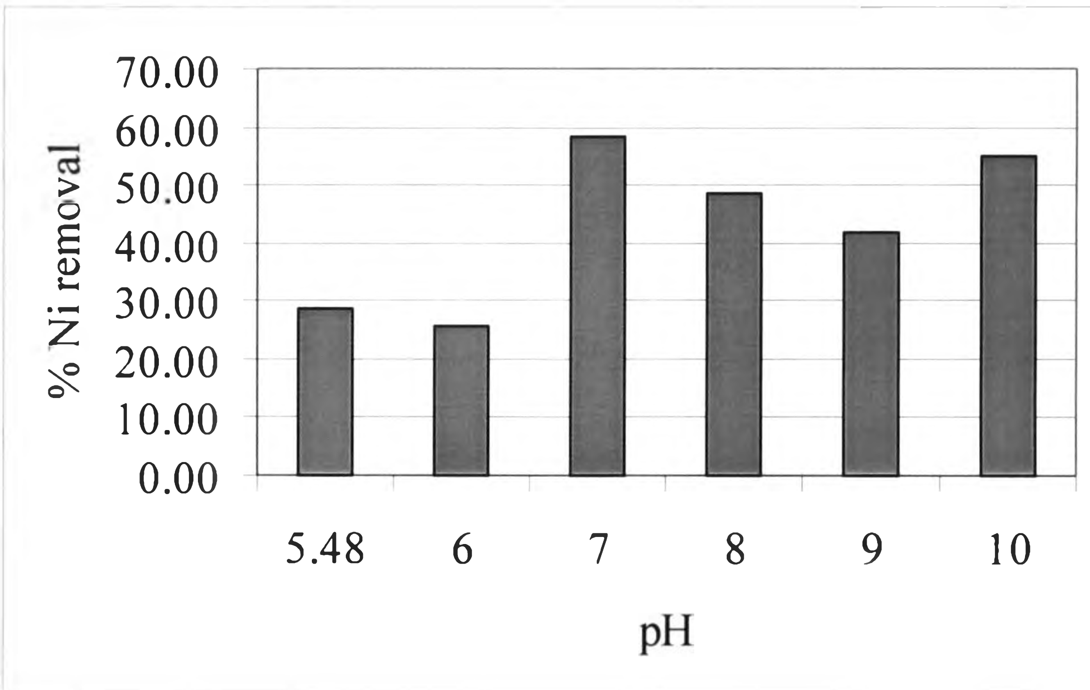

Figure 4.3 Effect of influent pH on nickel removal at 6.9 mg/L nickel concentration

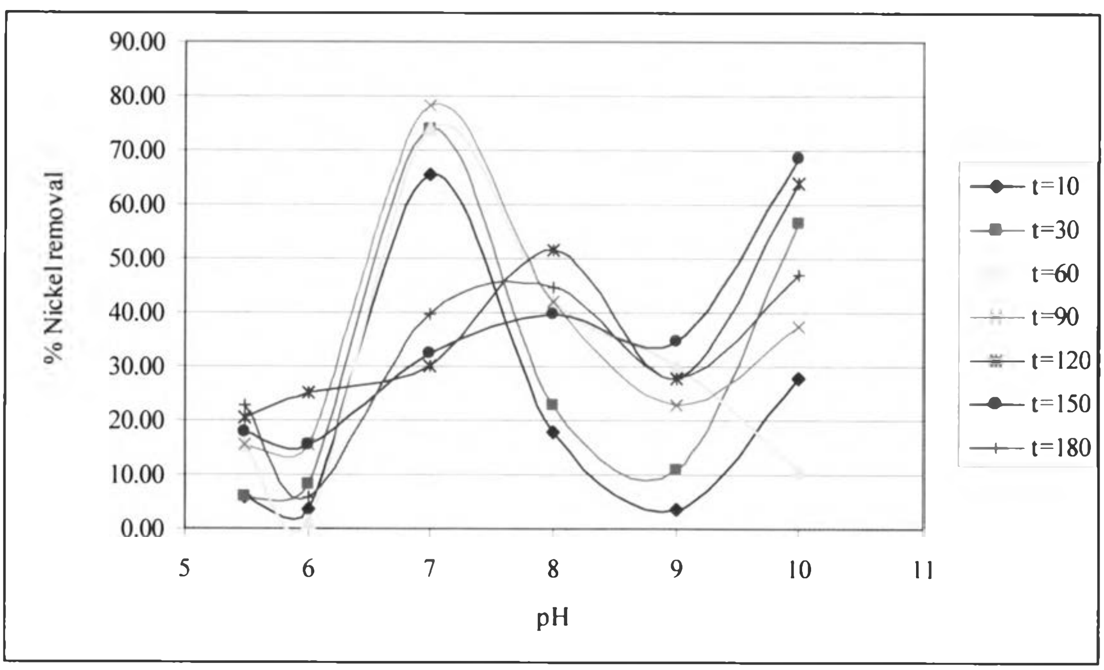

Figure 4.4 The relationship between nickel removal percentage and the influent pH in the first 200 minutes

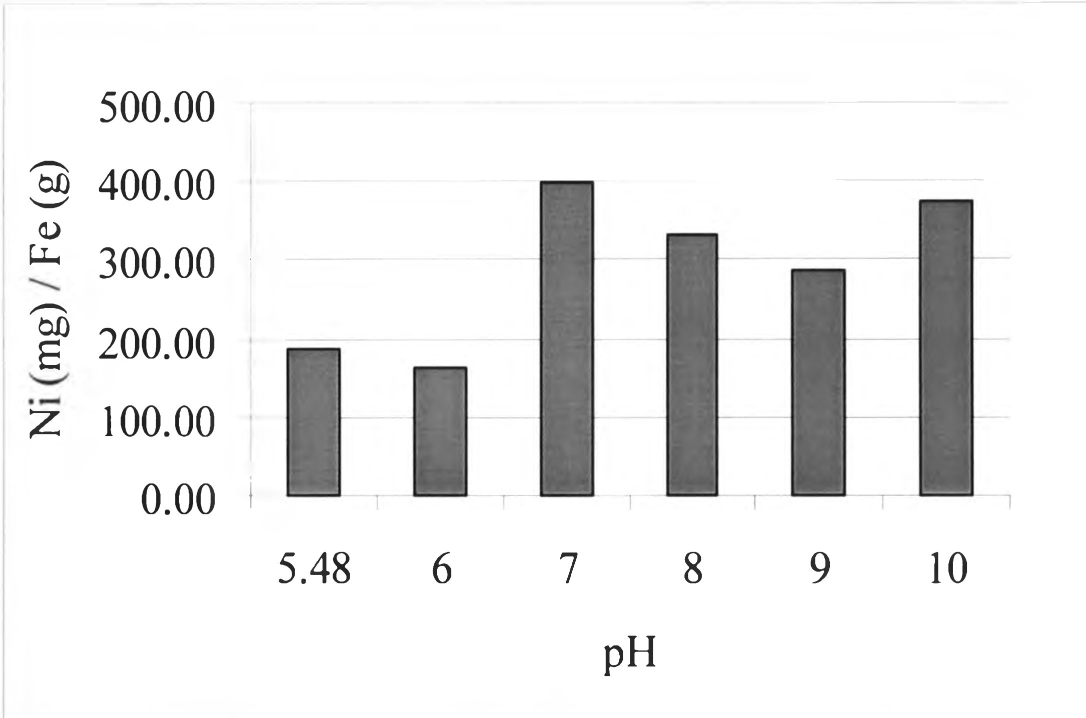

Figure 4.5 The relationship between nickel adsorbed per gram of iron and influent pH

4.4 Effect of column height on nickel removal efficiency

The next study was conducted at pH 7 with influent nickel concentration of 10 mg/L. Three adsorption columns were put in series and three column heights, 30 cm, 40 cm, and 50 cm were tested and the results are shown in Figures 4.6, 4.7, 4.8, and 4.9. These figures show that almost all nickel could be removed in the first 5 days. After 5 days, nickel concentration was fluctuated in the effluent. The longer the bench scale adsorption columns operated, the less efficiency they would have. The experimental results show that nickel adsorbed by iron oxide probably saturated in 5 days, after that, a cycle of desorption and adsorptions took place, which resulted in the fluctuation of nickel concentration in the effluent.

Three equations were obtained by using curve fitting to predict the nickel removal and they are shown in Table 4.2. The plots of nickel percentage removal versus time are shown in Figures 4.10, 4.11, 4.12, and 4.13.

Table 4.2 Using curve fitting to predict the nickel effluent concentration

Column height, 3 in series (cm)	Equation	Correlation coefficient, r^2
30	Y = 0.8153 Ln (X) – 0.4919	0.5251
40	Y = 0.7748 Ln (X) – 0.7972	0.5984
50	Y = 0.6990 Ln (X) – 0.5657	0.6290

where X is time in day and Y is effluent nickel concentration in mg/L.

The Department of Industrial Work, Thailand, requests that the nickel concentration in the waste discharge be less than 1 mg/L. All data in these three experiments were used and plotted in a diagram (Figure 4.14). It was found that only 12 % of the data obtained from the tests that had a column height of 30 cm and operated with 3 columns in series could reach a nickel concentration of less than 1 mg/L in the effluent. Whereas that data had effluent nickel concentrations of less than 1 mg/L for the column height of 40 cm with 3 columns in series and column height of 50 cm with 3 columns in series were 38 % and 29 %, respectively. The experiment results indicate that the three columns with a height of 40 cm each was the best setup among three experimental heights tested.

A statistic analysis was conducted on the experiment data for nickel percentage removal at steady state. The mean value of the removal efficiency for the column height of 40 cm operated with 3 columns in series was 89.4% and the standard deviation was 2.70. Whereas that the mean values of the removal efficiency for the column height of 30 cm and 50 cm, both operated with 3 columns in series, were 82.9% and 87%, respectively. Their standard deviations were 5.0 and 4.56, respectively.

One Way Anova was used to analyze the effect of column height on nickel removal. It was found that there is no significance difference in using three adsorption columns with a column height 40 cm or 50 cm. However, significant difference was found between the columns with the height of 40 cm and 30 cm. The correlation between 50 cm column height and 30 cm column height 30 cm was also significant. The One Way Anova analysis was conducted using a significant level of 0.05 (p-value).

The columns with a height of 40 cm had the optimum nickel removal. The columns with 40 cm height had more than 6.5% and 2.3% nickel removal than these with 30 cm and 50 cm column height, respectively. These results show that the increase of column height would increase nickel sorption. However, when the column height reaches 40 cm, further increase of column height would reduce nickel sorption. This could be due to the insufficient oxygen in the longer column, which resulted in incomplete iron oxidation and HFO sorption capacity. Column clogging was also observed in the 50-cm column height study.

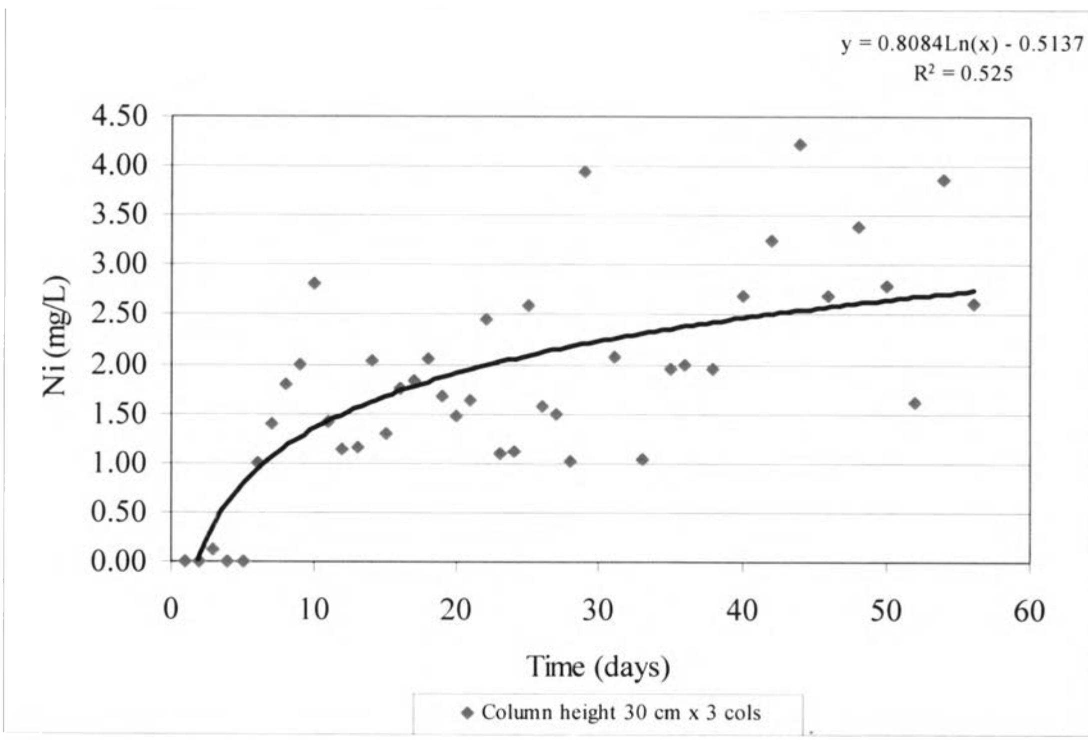

Figure 4.6 Effect of column height on nickel removal column hight = 30 cm. with 3 columns in series. Influent Ni = 10 mg/L and pH 7

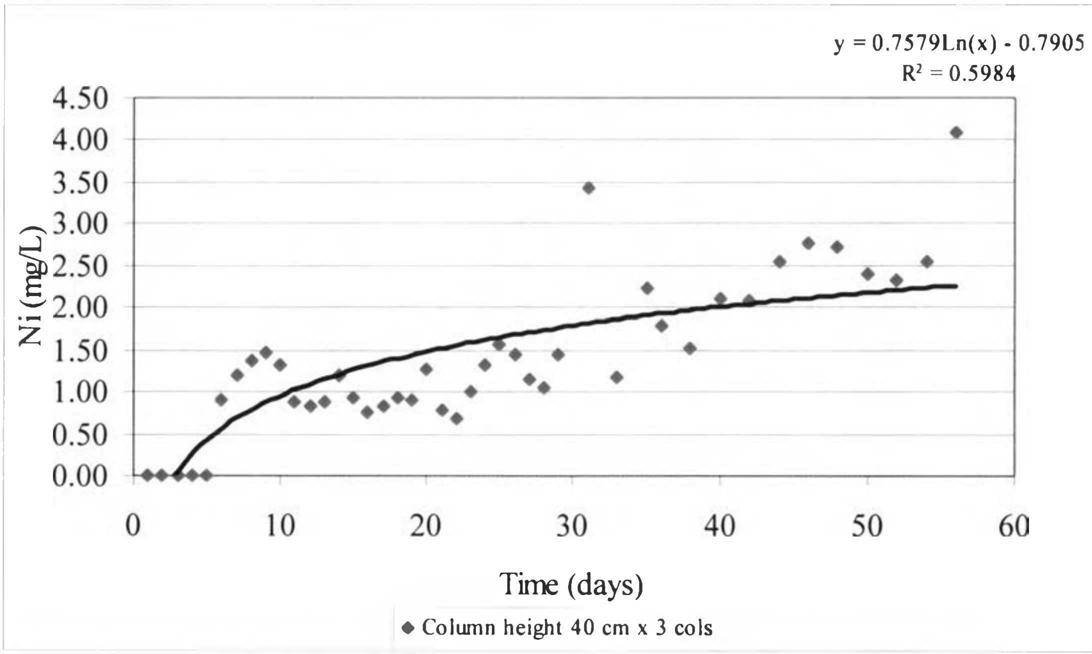

Figure 4.7 Effect of column height on nickel removal column hight = 40 cm. with 3 columns in series. Influent Ni = 10 mg/L and pH = 7

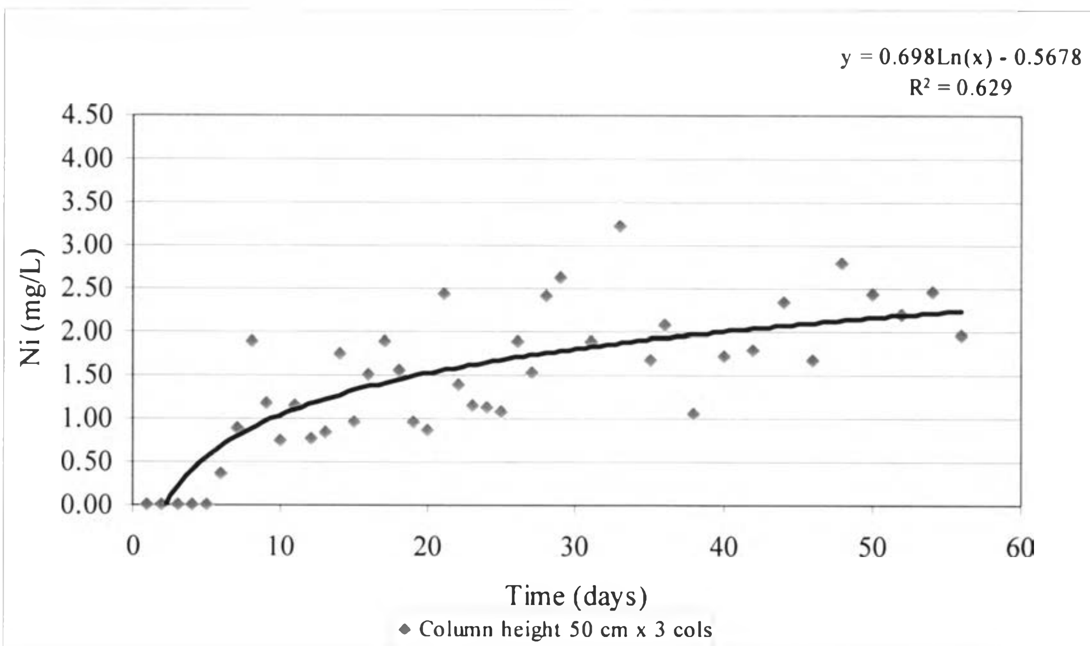

Figure 4.8 Effect of column height on nickel removal column height = 50 cm. with 3 columns in series. Influent Ni = 10 mg/L and pH = 7

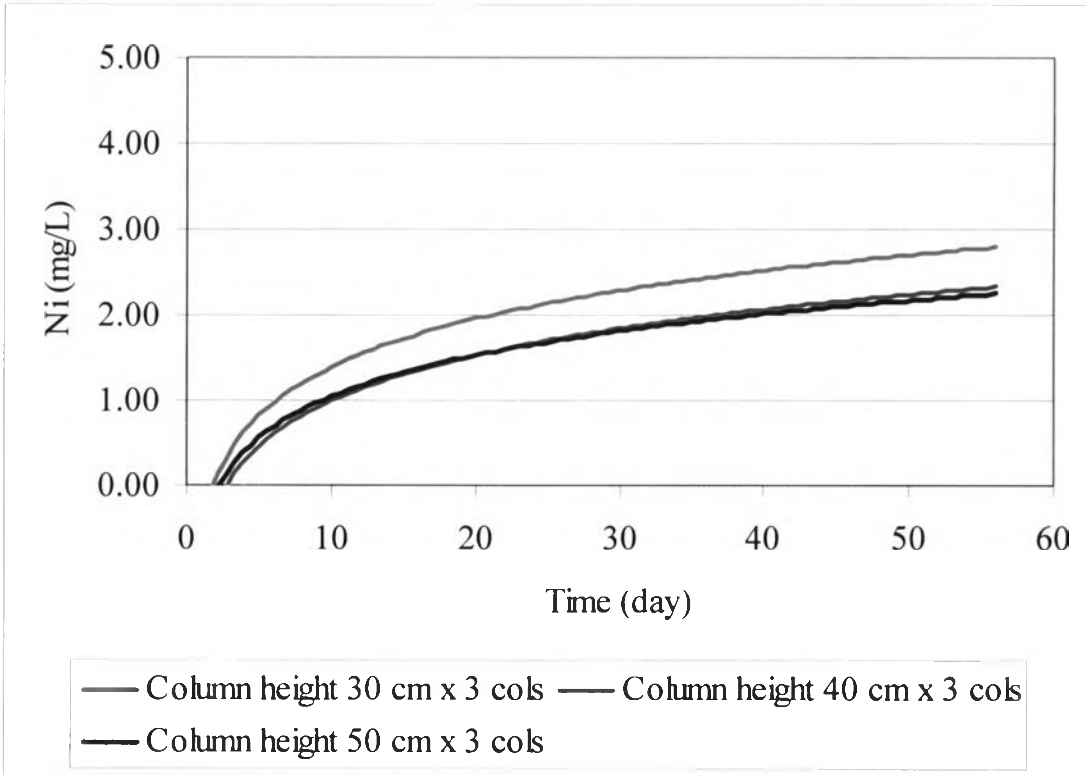

Figure 4.9 The relationship between Ni residue and time

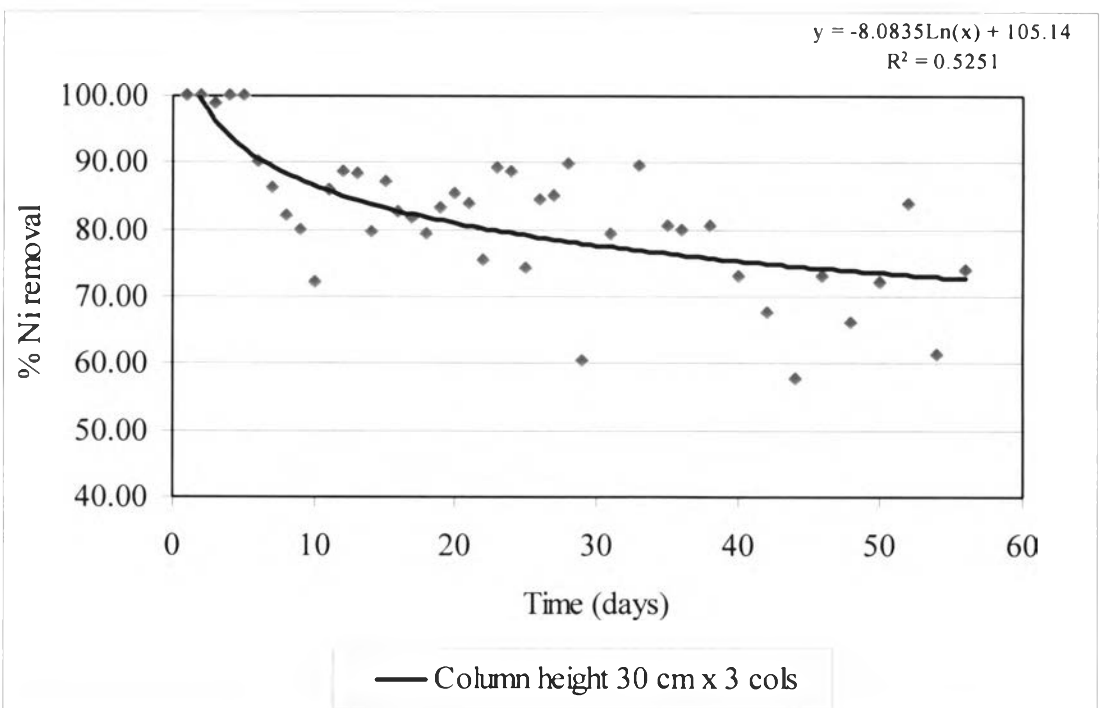

Figure 4.10 The relationship between Ni removal percentage and time for the column height 30 cm with 3 columns in series

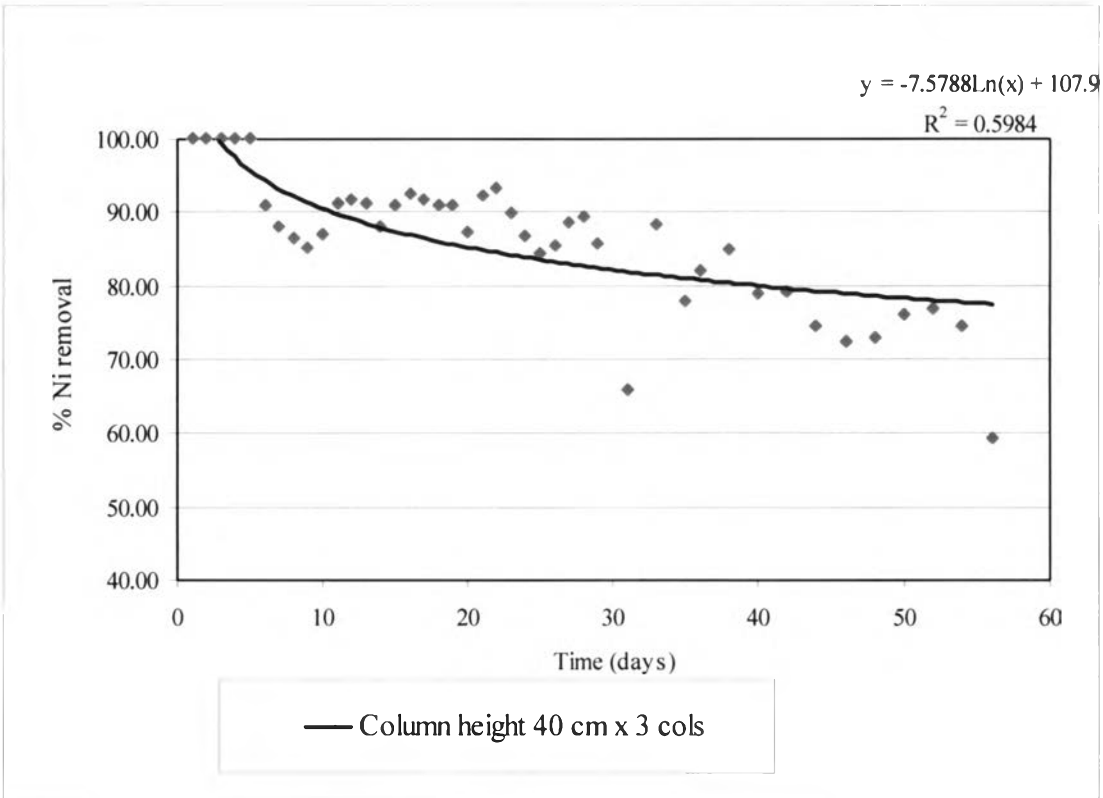

Figure 4.11 The relationship between Ni removal percentage and time for the column height 40 cm with 3 columns in series

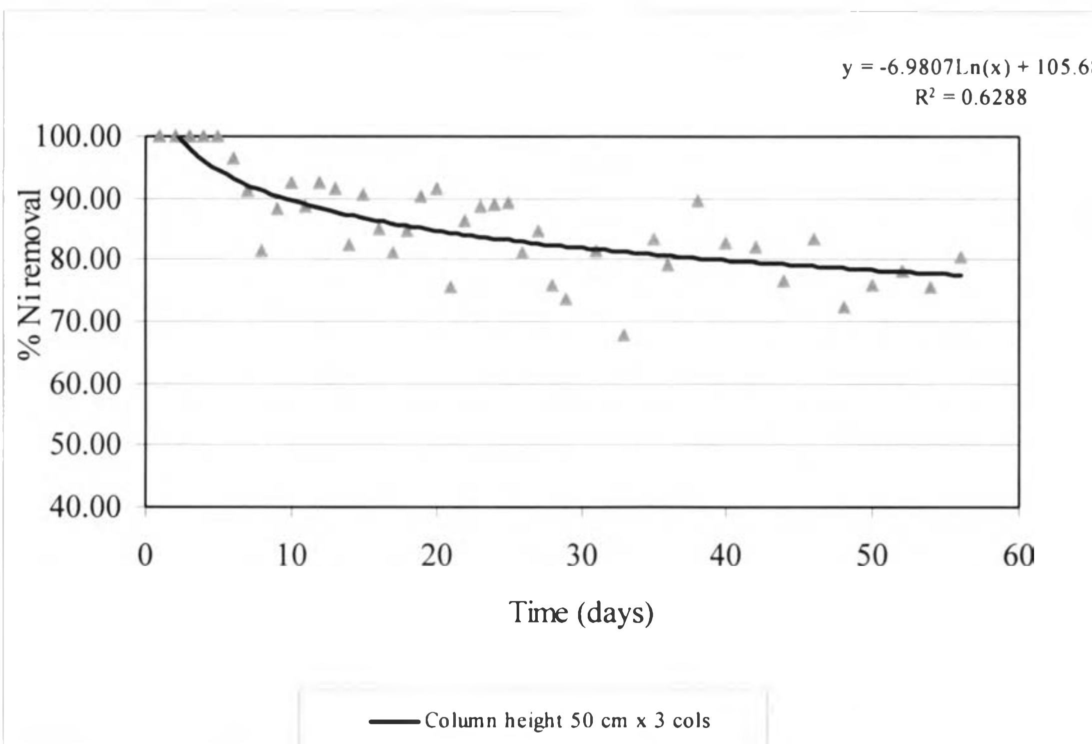

Figure 4.12 The relationship between Ni removal percentage and time for the column height 50 cm with 3 columns in series

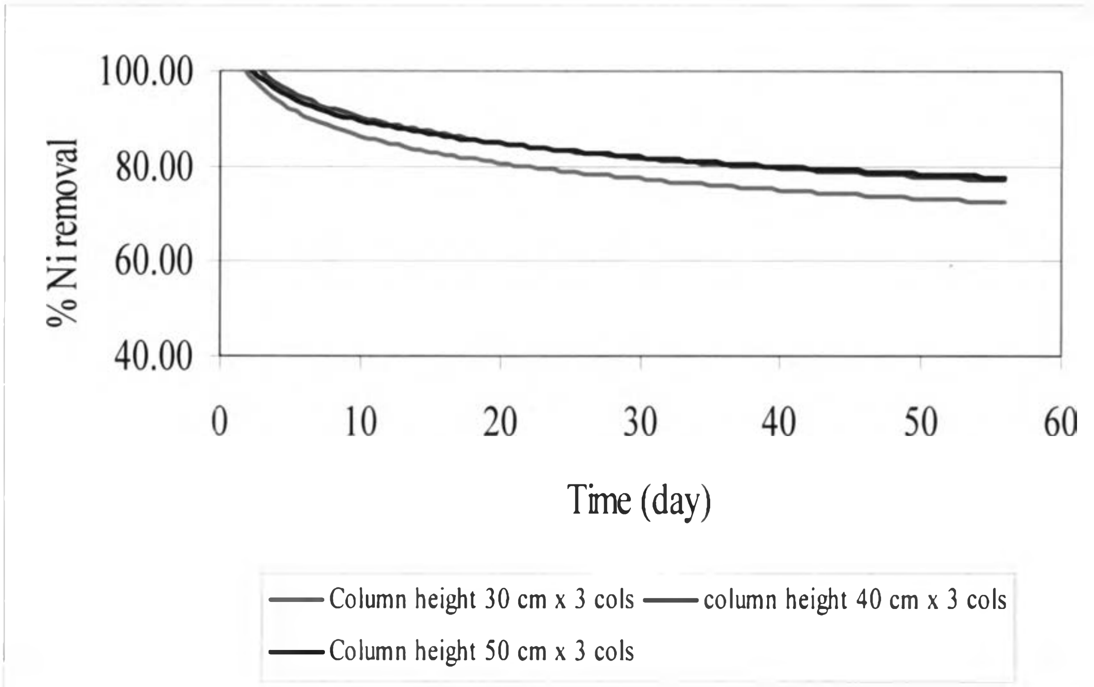

Figure 4.13 The relationship between Ni removal percentage and time for three series

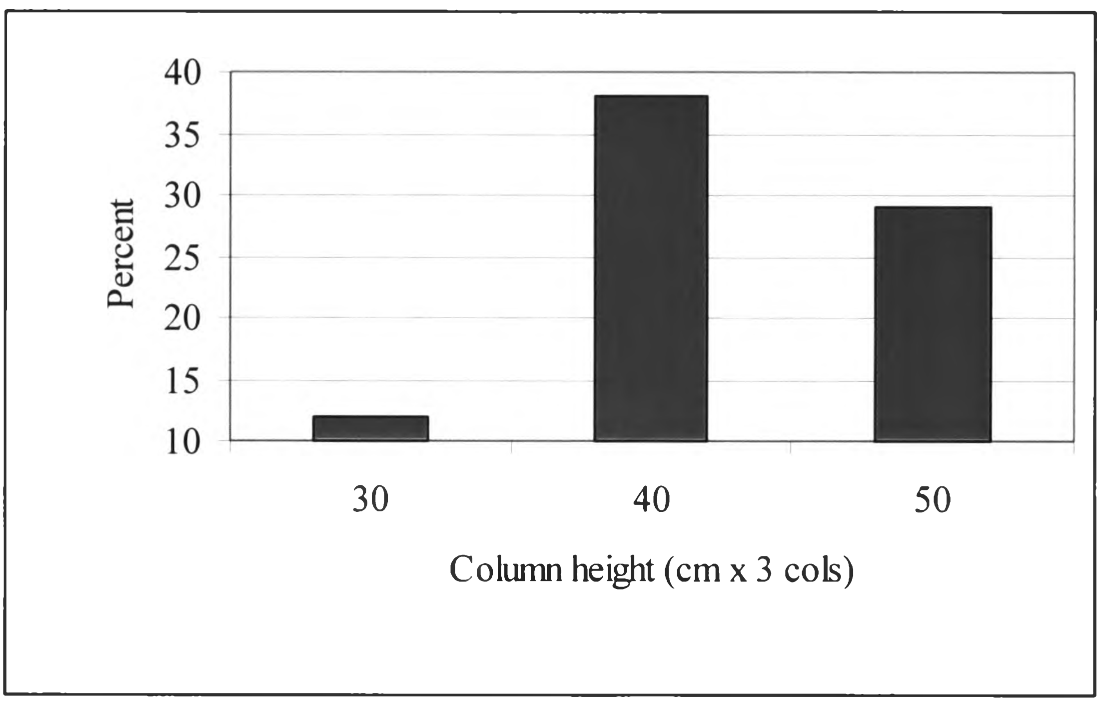

Figure 4.14 Nickel concentration less than 1 mg/L in the effluent
(Tested with 3 columns in series)

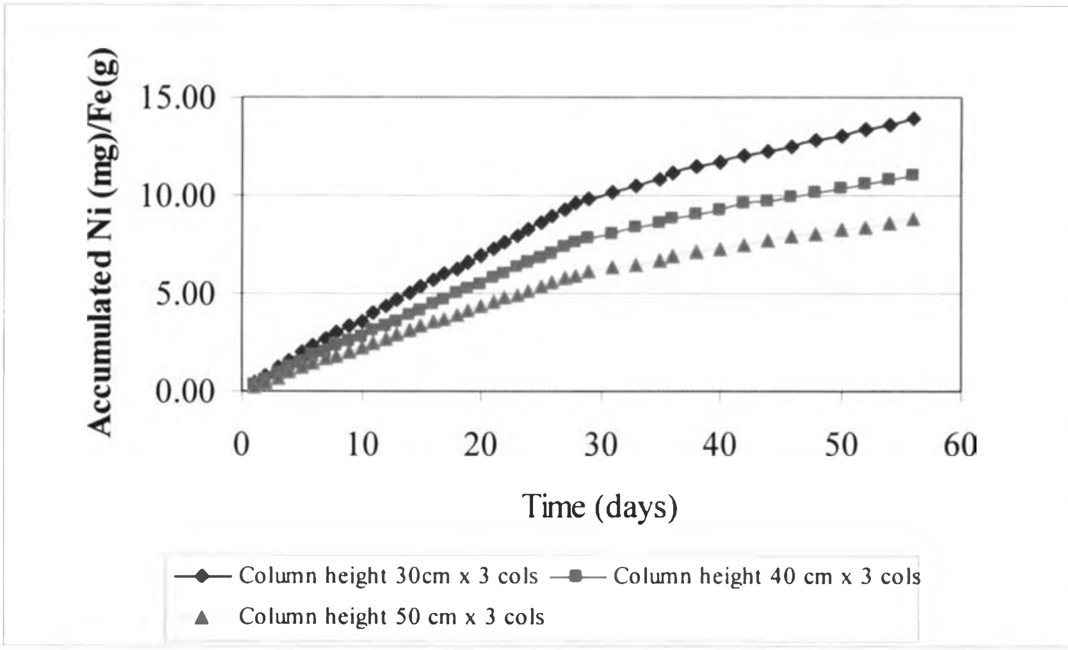

Figure 4.15 The relationship between accumulate Ni and time

An experiment to compare nickel adsorbed by iron oxide for different column height was performed. Three columns were put in series and three column heights, 30 cm, 40 cm, and 50cm were used. The operation time was 56 days. Influent nickel concentration was 10 mg/L and the influent flow rate was 10 liter per day. The results are shown in Figure 4.15. This figure shows the relationship between accumulated nickels (milligram/gram of iron) and time. The accumulated nickel for column height of 30 cm, 40cm, and 50 cm were 13.90 mg-Ni, 11.00 mg-Ni, and 8.76 mg-Ni, respectively. These results show that increase column height would reduce nickel sorption. This confirms that insufficient oxygen in the longer column, which resulted in incomplete iron oxidation and HFO sorption capacity (Ratanatamskul,1993).

4.5 Effect of influent flow rate on nickel removal efficiency

The wastewater was diluted to an influent nickel concentration of 10 mg/L and the diluted wastewater was used in this part of the study. The pH of the wastewater was adjusted to 7 by adding 0.1N HCl or 0.1 N NaOH. The effluent nickel concentration versus time at different influent flow rate is plotted in Figures 4.16, 4.17, 4.18, and 4.19. These figures show that the nickel concentration was not detectable in the effluent for the experiment with a flow rate 10 liter per day or 15 liter per day in the first 5 days. Whereas the nickel in the effluent for the experiment with a flow rate of 5 liter per day was not detectable in the first 10 days. After these period, the nickel concentration increased in the effluent. The longer the system operated, the less efficiency the columns would obtain. These experimental results show that the iron oxide column operated with a flow rate of 10 liter per day or 15 liter per day were probably saturated with nickel in 5 days. Whereas the columns with a flow rate 5 liter per day were saturated with nickel in 10 days. After these days, cycles of desorption and adsorptions occurred.

Calculation was conducted to determine the nickel removal percentage in the three flow rates tested. The relationship between the nickel removal percentage and the flow rate are shown in Figures 4.20, 4.21, 4.22, and 4.23. Removal percentage of 86.27%, 84.92%, and 75.80% were obtained for the flow rate 5 liter per day, 10 liter per day, and 15 liter per day, respectively. MS Excel was used to perform curve fitting to predict the nickel concentration in the effluent. Three equations obtained are shown in Table 4.3.

Table 4.3 Prediction of nickel concentration in effluent in terms of flow rate

Influent flow rate Liter per day	Equation	Correlation coefficient, r^2
5	Y = 0.7859 Ln (X) – 1.0092	0.7143
10	Y = 0.7803 Ln (X) – 0.8590	0.6287
15	Y = 1.0373 Ln (X) – 0.7074	0.7514

where X is time in day and Y is effluent nickel concentration (mg/L)

A statistic analysis was conducted to determine the nickel removal percentage at different flow rate at steady state. An average 91.6% removal with a standard deviation of 4.53 can be obtained for the 5 liter per day flow rate. The mean removal efficiency of 90.0% with a standard deviation of 2.03 can be obtained for the flow rate of 10 liter per day. The average nickel removal for the influent flow rate of 15 liter per day was 81.5% with a standard deviation of 3.58.

One Way Anova was used again to analyze the data. By comparing the data, no significant difference was found between flow rate 5 liter per day and 10 liter per day. The correlation between influent flow rate 5 liter per day and 15 liter per day were significant and the relationship between influent flow rate 10 liter per day and 15 liter per day were also significant. The percentage nickel removal for the flow rate of 5 liter per day was highest among three flow rates tested. Its removal was 1.6% and 10.1% higher than that of the experiments with a flow rate of 10 liter per day and 15 liter per day, respectively. This is because smaller flow provides longer contact time between wastewater and iron oxide. By comparison, the difference of 1.6%, nickel removal between the flow rate of 5 liter per day and 10 liter per day, was small, it implies a maximum flow rate 10 liter per day can be used in wastewater treatment.

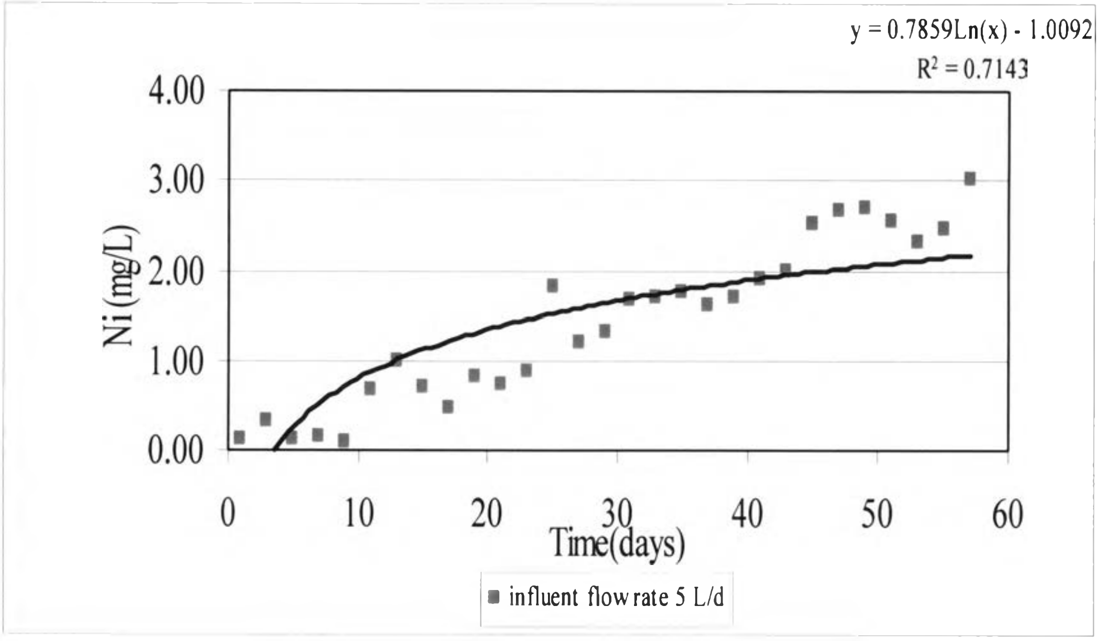

Figure 4.16 Effect of influent flow rate 5 L/d on Ni removal efficiency

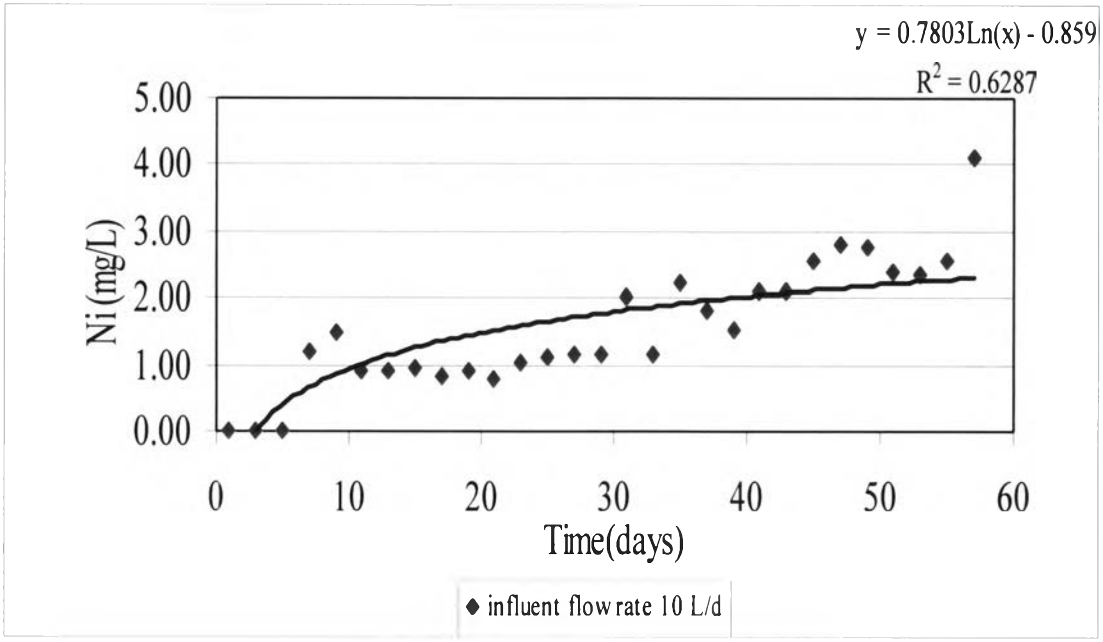

Figure 4.17 Effect of influent flow rate 10 L/d on Ni removal efficiency

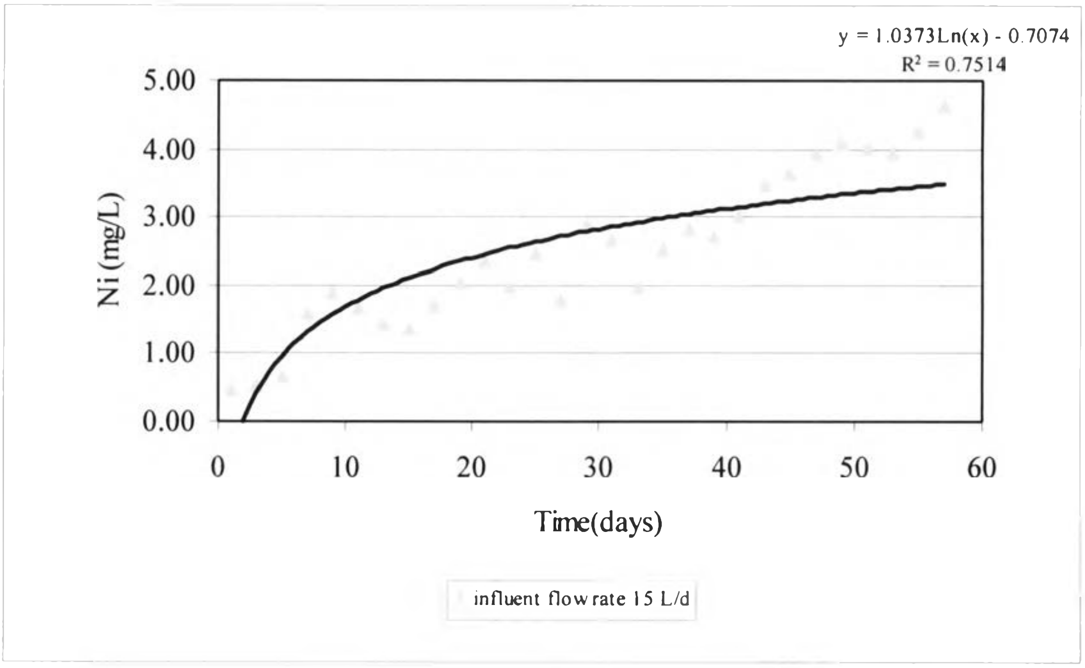

Figure 4.18 Effect of influent flow rate 15 L/d on Ni removal efficiency

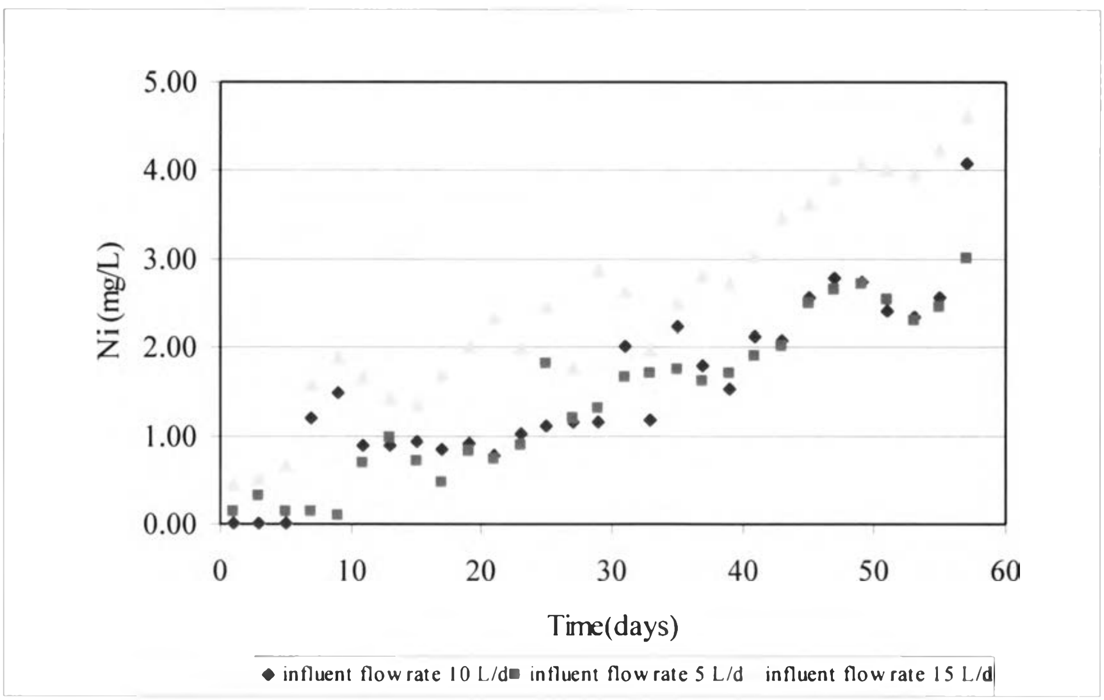

Figure 4.19 The relationship between Ni residue and time for three influent flow rate

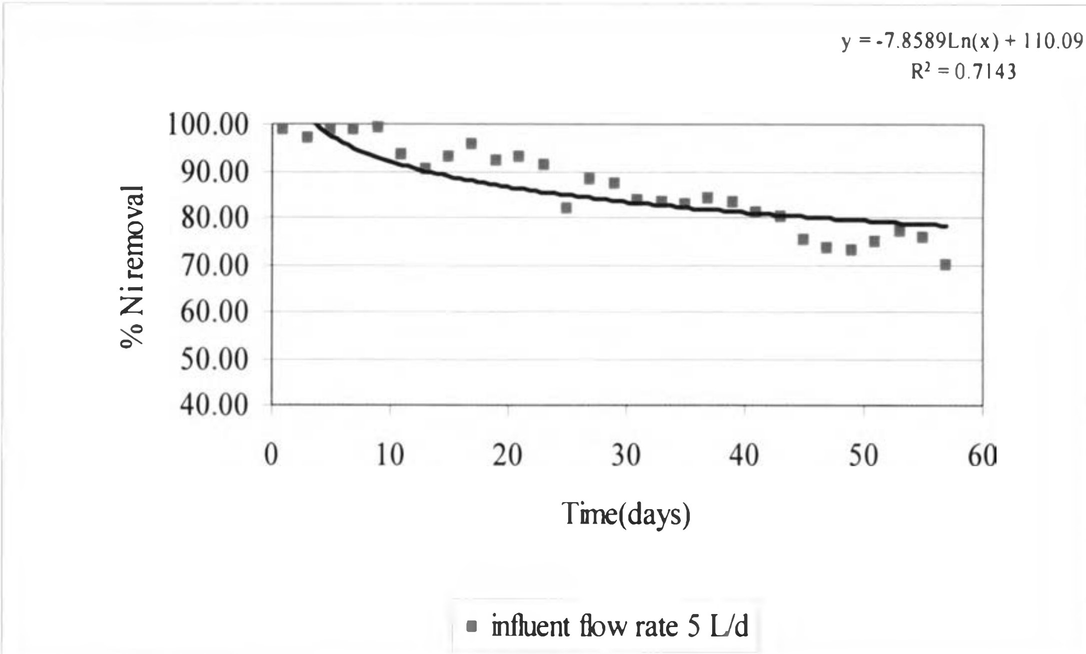

Figure 4.20 Effect of influent flow rate 5 L/d on Ni removal efficiency

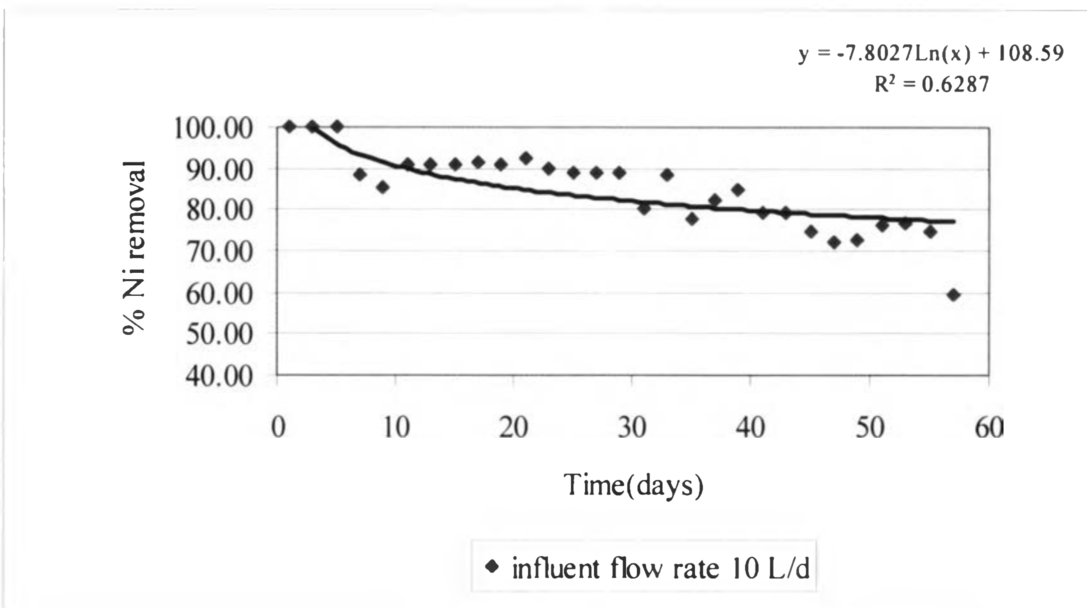

Figure 4.21 Effect of influent flow rate 10 L/d on Ni removal efficiency

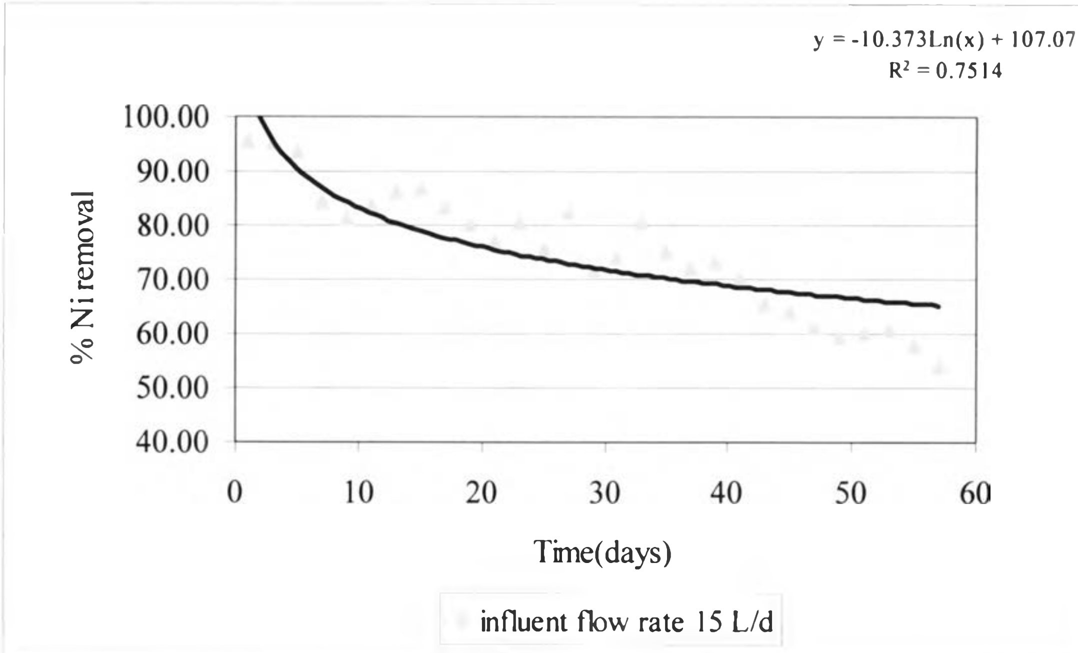

Figure 4.22 Effect of influent flow rate 15 L/d on Ni removal efficiency

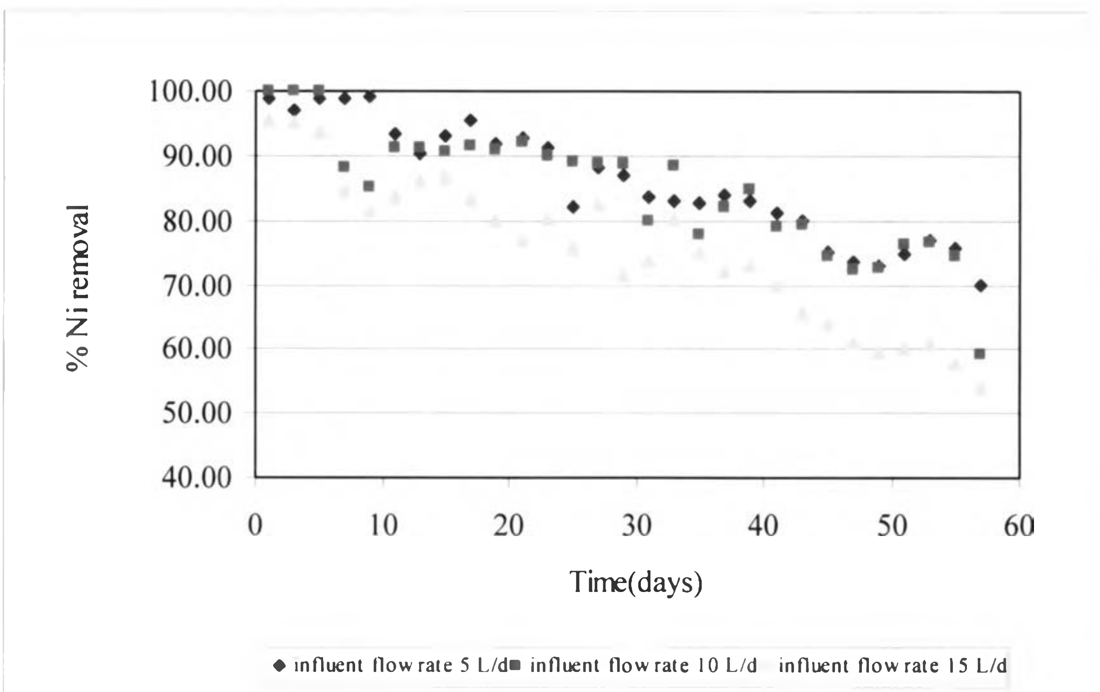

Figure 4.23 Effect of influent flow rate on Ni removal efficiency

4.6 Effect of nickel concentration on column performance

These studies were conducted at pH 7 with influent flow rate of 10 liter per day. Three columns, each with a height of 40 cm were used in this study. Three nickel concentrations in wastewater were tested: 20, 50, and 100 mg/L. The results along with these obtain for influent nickel concentration of 10 mg/L (Section 4.4) are shown in Figure 4.24. This figure shows that the highest nickel removal, close to 100%, took place at the influent nickel concentration of 10 mg/L in the wastewater. When the influent nickel concentrations were 20, 50 mg/L and 100 mg/L, the percentage removal were 93%, 84% and 62%, respectively. The figure also shows lower nickel percentage removal occurred at longer operation time, which was the same as those observed in earlier experiments. The longer the system operated, the less nickel removal percentage would get. From all the experiments conducted, the optimum operation condition would be at an influent flow rate of 10 liter per day with an influent nickel concentration 10 mg/L and a pH of 7; and to operate the treatment system with 3 iron columns in series.

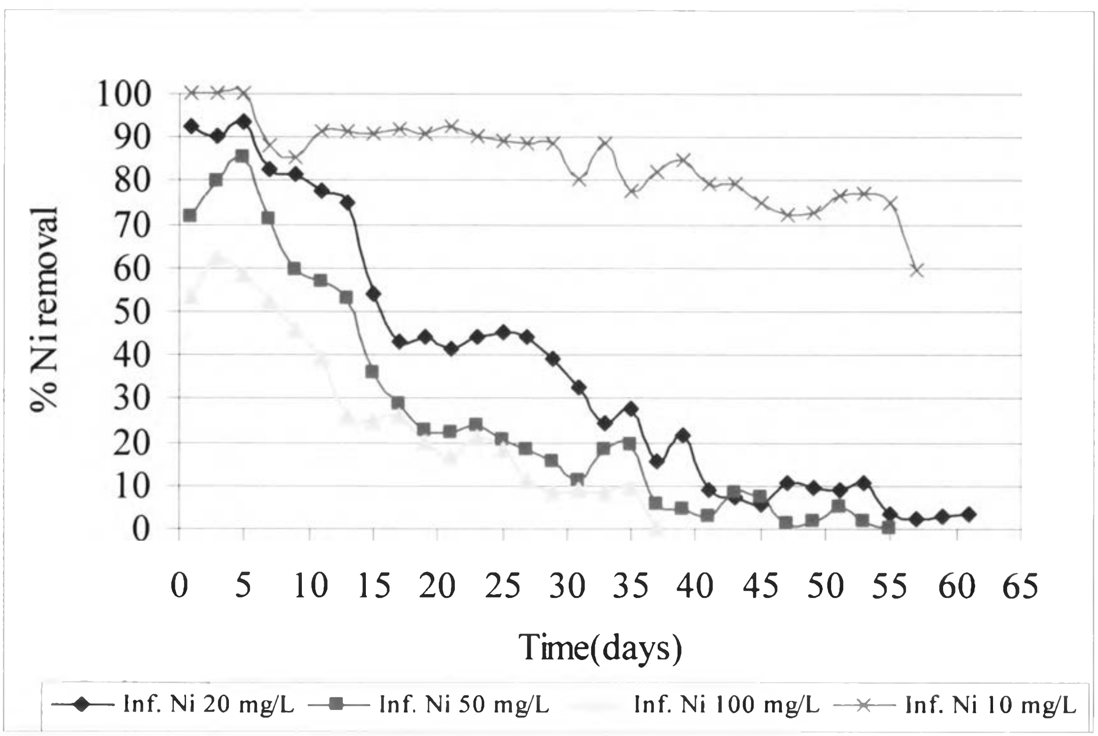

Figure 4.24 Effect of nickel concentration on column performance

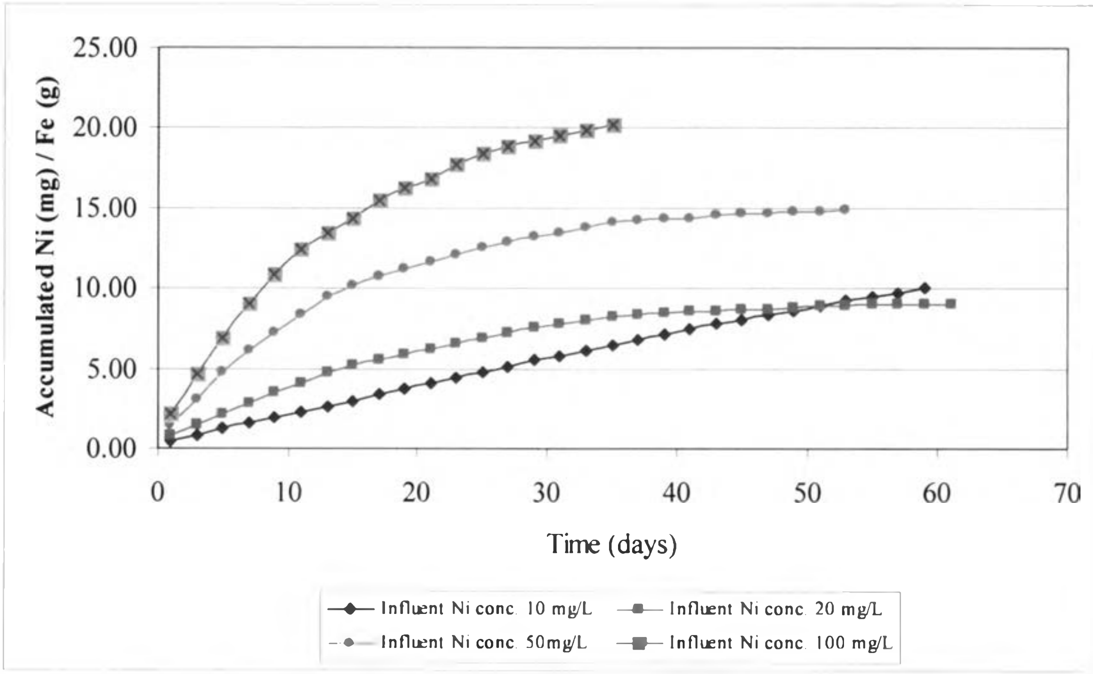

Figure 4.25 The relationship between accumulate Ni and time.

Calculation was conducted to determine the nickel accumulated (milligram/gram of iron) at four influent nickel concentrations, 10, 20, 50, and 100 mg/L. The results are shown in Figure 4.25. This figure shows that the maximum nickel sorption for influent nickel concentrations, 10, 20, 50, and 100 mg/L were 10.07, 9.04, 14.83, and 20.15 mg-Ni per gram iron, respectively. These results show that the increase of influent nickel concentration would increase nickel sorption. However, columns clogging occurred on 55 days of the operation at influent Ni concentration 50 mg/l and on 37 days at influent nickel concentration 100 mg/L. For the influent nickel concentration 10 mg/L, the longer the system operated, the more nickel adsorbed. For the influents nickel concentration 20 mg/L, nickel adsorption stayed the same after 37 days.

4.7 X – Ray Diffraction (XRD)

Structure of iron material was analyzed with an X – Ray Diffraction Spectrometer. The diffractograms of iron material before and after reaction with nickel are shown in Figures 4.26 and 4.27. It was found that the signal intensities were 382 and 667 for the peaks of iron materials before and after reaction with nickel, respectively. An increase in the signal intensities supports that nickel could be adsorbed with the iron oxide. The possible structure of the complex might be $NiFe_2O_4$ with NiO.

4.8 Proposed design criteria for iron scrap column

From the continuous flow experimental, the nickel-loading rate can be

calculated by the following equation.

$$\text{Nickel loading rate} = (Q \times C) / A \qquad (4.6)$$

Where Q is flow rate in litter per day,

C is influent nickel concentration in mg/L, and

A is cross sectional area.

The nickel-loading rate was obtained as shown in Table 4.4

Table 4.4 Nickel loading rate on column performance

Influent Ni concentration. (mg/L)	Flow Rate (L/day)	Packing density of iron oxide (g/cm^3)	Ni loading rate (kg/m^2 day)
10	10	2.8	0.203
20	10	2.8	0.408
50	10	2.8	1.020
100	10	2.8	2.040

* Column clogging observed.

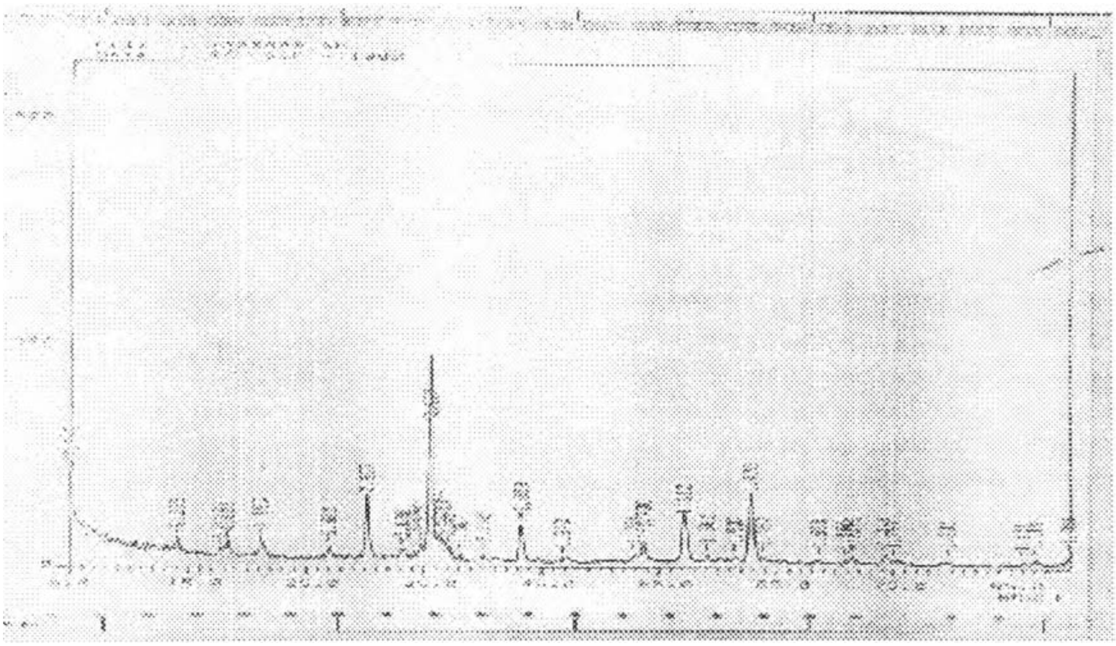

Figure 4.26 The diffractogram of iron material before reaction with nickel

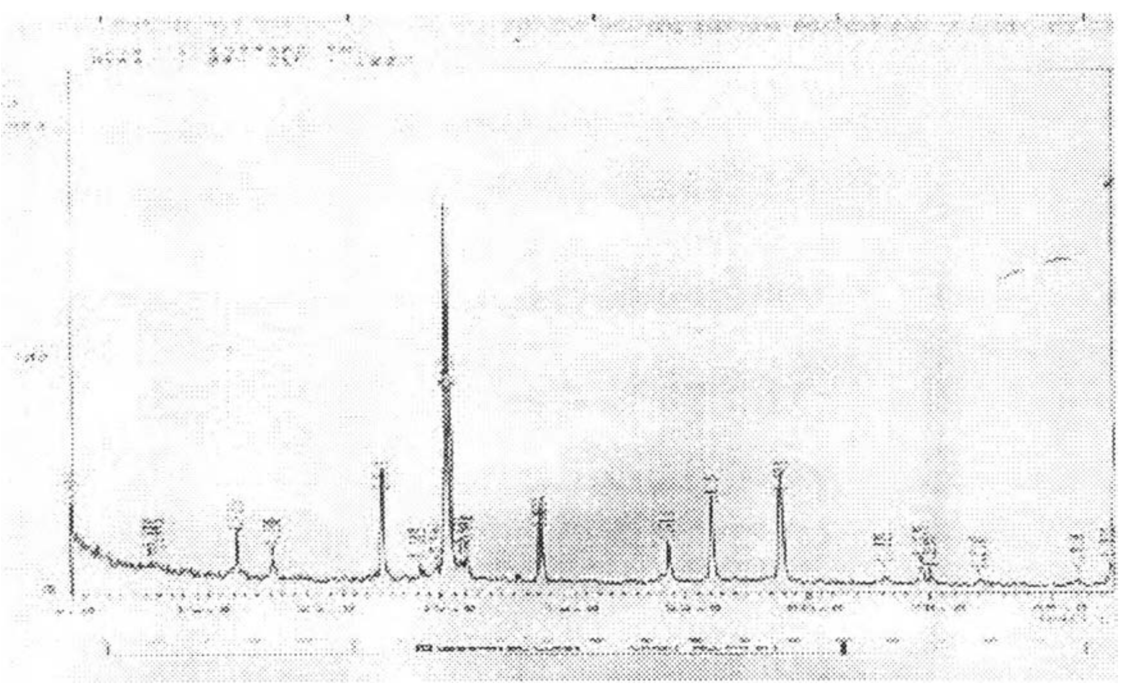

Figure 4.27 The diffractogram of iron material after reaction with nickel