REMOVAL OF NICKEL FROM METAL PLATING WASTEWATER BY LOW-COST IRON SCRAP COLUMN

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ABSTRACT

Removal of nickel from metal plating wastewater by iron scrap column was investigated in this study. Both batch experiment and continuous flow experiment were conducted. The batch experiment was performed to determine adsorption isotherm together with effect of pH on nickel removal efficiency. The continuous flow experiments was used to study effects of column height, influent flow rate, and feed nickel concentration on column performance. The pH was an important factor affecting nickel removal by iron scrap. The maximum nickel adsorption by hydrous ferric oxide (HFO) occurred in the neutral and slight ly alkaline range. The continuous flow experiment was conducted with a two-month operation period. Three columns were placed in series, having each column height of 30 cm, 40 cm, and 50 cm. The test with column height 30 cm could yield the highest adsorption capacity. Longer column height would increase nickel removal percentage but less adsorption capacity in terms of mgNi./g Fe. This might be due to more oxygen depletion in longer columns, then less hydrous ferric oxide on iron scrap's surface could be effectively formed. Three flow rates of 5, 10 and 15 L/d, were tested and nickel removal efficiencies were 86.27%, 84.92%, and 75.80%, respectively. Higher influent flow rate tended to decrease removal efficiency. Moreover, the study of the effect of nickel concentration on column performance, the maximum nickel sorption were 10.07, 9.04, 14.83, and 20.15 mg-Ni/gram iron for influent nickel concentrations at 10, 20, 50, and 100 mg/L, respectively. Therefore, iron scrap column can be alternative technology to recover nickel from metal plating wastewater.

KEYWORD : Iron scrap, nickel, adsorption, metal plating wastewater

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INTRODUCTION

Metal Plating industry is recognized as one of main sources that discharge wastewater containing high amount of heavy metals into environment. Metal plating wastewater containing significant inorganic contaminants is frequently treated by precipitation process. Precipitation process includes solution pH adjustment to neutral or alkaline range and then

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precipitating of insoluble species. This procedure usually results in efficient removal of insoluble contaminants. The expenditures in this process include the excess alkaline reagent to neutralize the acid, and handling and disposal of the sludge produced. Also, the associated labor, operation, maintenance, and transportation expenses have put financial burden to the industry. The production of sludge also add hidden long-term societal cost associated with the depletion of the limited landfill capacity. Therefore, an improved treatment technology is needed in this area.

Utilization of oxide of heavy metals to remove dissolved contaminants is based on the principle of adsorption/precipitation of these impurities with oxide of metals. The making of this adsorbent involves the treating of the waste with hydrous ferric oxide (HFO) that is formed on the surface of iron scrap. HFO is an amorphous adsorbent and has particle sizes ranging from 1 to 10 nm. It is highly porous and resembles a swollen gel, rather than a homogeneous solid. HFO has a formula of Fe_2O_3 nH_2O (n varies from 1 to 3). The density varies from 2.2 to 4.0 g/cm^3, with an average of 3.5 g/cm^3. HFO removes dissolved contaminants by surface adsorption and precipitation, and through precipitate formation linked to subsequent sedimentation which sweeps material from suspension (sweep flocculation).

HFO, which can also be formed from the beneficial reuse of iron waste, has also been successfully employed to reduce the concentration of hazardous contaminants and potentially valuable metallic elements (As, Se, Cu, Cr, and Zn) in a variety of waste streams (Benjamin and Leckie, 1981; Benjamin, 1983; Merrill et al., 1985, Brooks, 1990). The advantage of using HFO in waste treatment is its low cost and its ability to modify the treated sludge's characteristics to meet the non-hazardous waste criteria.

Nickel is commonly used in metal plating industry. Thus, metal plating wastewater is usually contaminated with high concentrations of nickel. This study has concentrated on the removal of nickel (Ni) with hydrous ferric oxide inside iron scrap column. To reduce the treatment cost, waste iron was selected as an adsorbent. This process aims to minimize chemicals and sludge disposal costs. The goal of this work was to study and develop an alternative wastewater treatment technology for the metal plating industry.

METHODOLOGY

The size of iron scrap was cut to about 4.4 mm x 6.5 mm x 0.1 mm. The iron scrap was pretreated with 0.01 N-HCl solution to remove oil from its surface. It was then dried for about 4 weeks in room temperature to form hydrous ferric oxide as the rust on iron scrap's surface. Five experimental investigations were performed as follows;

1. Nickel adsorption on hydrous ferric oxide (HFO)

In the batch experiment, 2 grams of iron scrap were added to flask. Each flask contained 200 ml wastewater. The concentration of nickel in the wastewater was 6.9 mg/L, which had been diluted from the wastewater collected from the industry. The flasks, then were shaken in room temperature until reaching steady state condition. The nickel concentrations in the supernatant were analyzed with an atomic absorption spectrometer (Perkin Elmer, AA Model 2380) at the reaction times 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 300, 420, 540, 660, 900, 1020, 1140, 1260, 1380, and 1500 minutes, respectively. The nickel removal percentages were then plotted versus reaction time.

2. Effect of pH on nickel removal

Another batch experiment was carried out to study the effect of pH on hydrous ferric oxide sorption of nickel. The concentration of nickel was 6.9 mg/L and the experimental set up was identical to that of the previous experiment. The pH of the tested samples was adjusted to 6, 7, 8, 9, and 10, respectively, by adding 0.1 N HCl or 0.1 N NaOH. The sample bottles were shaken in room temperature until reaching steady state condition. The nickel concentrations in the supernatant were analyzed with the same previous method at the reaction times 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 300, 420, 540, 660, 900, 1020, 1140, 1260, 1380, and 1500 minutes, respectively. The nickel removal percentages were then plotted versus pH.

3. Effect of column height on nickel removal efficiency

Bench-scale adsorption columns were fabricated for continuous flow experiments. The column is 2.5 cm in diameter and it was filled with waste iron scrap. The iron packing density was 2.8 g/cm^3. Three columns were put in series. Three column heights, namely, 30cm, 40cm, and 50cm, were tested. The testing apparatus is shown in Figure 1. Wastewater was diluted to have a nickel concentration of 10 mg/L. It was found in the previous experiment that the optimum pH for nickel adsorption was 7 and the solution pH was maintained at 7 by adding 0.1 N HCl or 0.1 N NaOH. The wastewater was pumped to an elevated water tank, which was placed on the top of a rack. The wastewater was fed to the top of the first column, then it went through the columns by gravity. The flow rate was controlled at 10 liter per day by using a valve. The effluent from the last iron scrap column was sampled and nickel concentrations were analyzed with the same previous method. The nickel percentage removal was then plotted versus column height.

4. Effect of influent flow rate on nickel removal efficiency

The purpose of this experiment was to determine how influent flow rate would affect iron removal in continuous flow condition. Bench-scale adsorption columns were fabricated. The column is 2.5 cm in diameter and it is filled with waste iron scrap. The iron packing density is 2.8 g/cm^3. The column height, which previously achieved the best nickel removal was used here. The wastewater was diluted to have a nickel concentration of 10 mg/L and the pH was maintained at 7. The wastewater was again pumped to an elevated water tank and then fed to the top of the first column and went through all three columns by gravity. Three flowrates were tested, 5 , 10 and 15 liters per day. The effluent from the last column was sampled and nickel concentrations were analyzed with an atomic absorption spectrometer. The nickel percentage removal was then plotted versus flow rate.

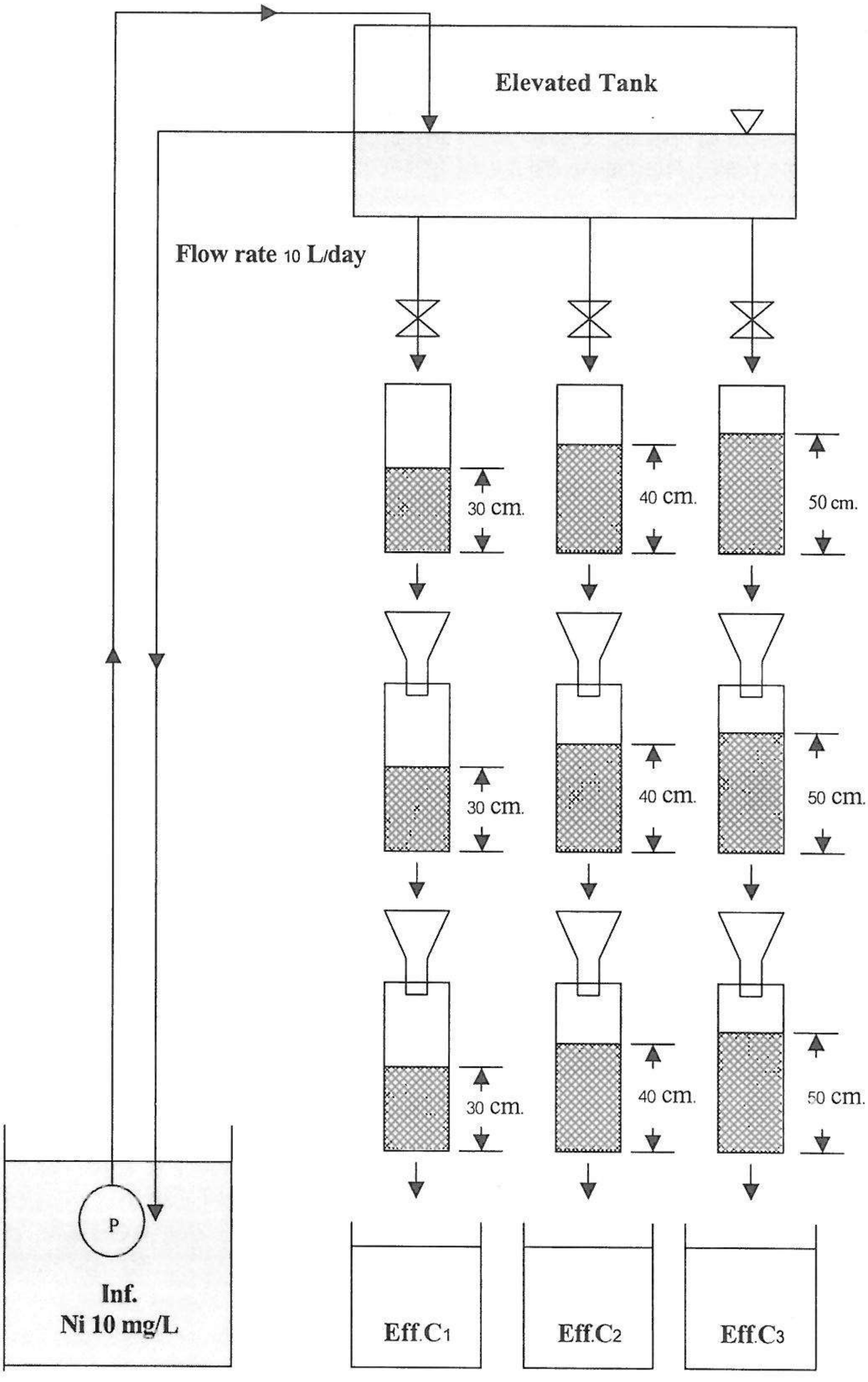

Figure 1 Experimental set-up for the study of the effect of column height on nickel removal

5. Effect of nickel concentration on column performance

Three units were used in this study. The optimum column height and flow rate obtained from previous experiments were used in this experiment. To study the effect of nickel loading on adsorption performance, the nickel concentration in wastewater was diluted to three concentrations in this study as 20, 50, and 100-mg/L. The pH was maintained at 7. Wastewater was pumped to an elevated water tank and then directed to the iron scrap column. Samples were taken from the columns effluent and nickel concentrations were measured.

RESULTS AND DISCUSSION

Adsorption isotherm

Here, the adsorption isotherm for nickel adsorption by hydrous ferric oxide (HFO) on the surface of iron scrap was determined. The isotherm seemed to follow Freundlich isotherm equation as $q = K \times C^n$. K and n values obtained from the experiments were 0.112 and 0.63, respectively ($R^2 = 0.981$). Then, Freundlich isotherm equation is expressed as

$$q = 0.1122C^{1/0.63} \quad (1)$$

Where C is the concentration of nickel after adsorption by HFO, q is the mass of nickel adsorbed per mass of iron scrap.

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 2. The reaction between nickel and iron oxide was rapid in the first 200 minutes. After this period adsorption rate became slow. The HFO could remove more than 60 % of nickel in wastewater if enough reaction time was given.

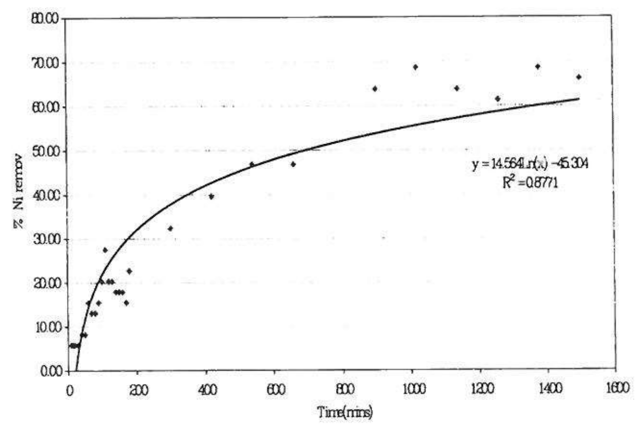

Figure 2 Adsorption of nickel with HFO

$$Y = 14.564 \ln(X) - 45.304 \quad (2)$$

$$R^2 = 0.8771$$

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

Effect of pH on nickel removal percentage

The influent had nickel concentration of 6.9 mg/l. in this study. The pH was adjusted to the pre-determined value by adding 0.1N HCl or 0.1 N NaOH. The relationships between nickel adsorbed in milligram per gram of iron and pH is shown in Figure 3. 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. A decrease in nickel removal at lower pH was probably caused by the release of nickel ions from surface of iron scrap due to increasing metal solubility at lower pH range. Therefore, it is recommended that the removal of nickel with iron oxide should maintain solution pH in neutral or slightly alkaline range. The hydroxyl group was the dominant adsorbable species in the pH range of 7 to 10 for nickel adsorption by HFO on surface of iron scrap.

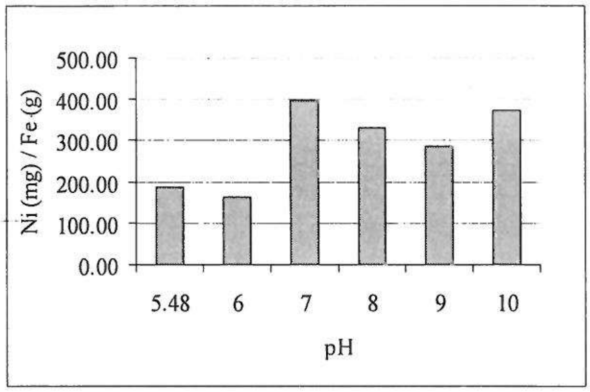

Figure 3 The relationships between nickel adsorbed per gram of iron and influent pH

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 columns were put in series and three column heights, 30 cm, 40 cm, and 50 cm were tested.

An experiment to compare nickel adsorbed by HFO for different column height was performed. The operation time was 56 days. Influent flow rate was 10 liter per day. The results are shown in Figure 4. This figure shows the relationships between accumulated nickel(milligram/gram of iron) and time. The accumulated nickel for column heights of 30, 40, and 50 cms were 13.90 , 11, and 8.76 mg-Ni/g Fe, respectively. These results show that an increase in column height tended to reduce nickel sorption capacity. This might be due to the depletion of hydrous ferric oxide on iron scrap's surface inside longer column, which resulted in incomplete iron oxidation and HFO sorption capacity (Ratanatamskul,1993 and 2002).

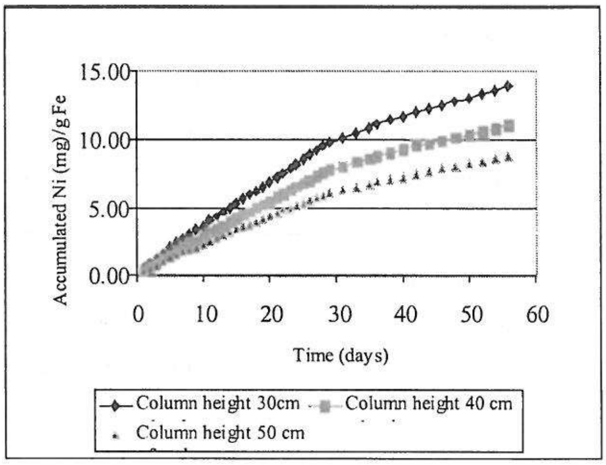

Figure 4 Effect of column height on amount of Ni accumuled on surface of iron scrap

Effect of influent flow rate on nickel removal efficiency

The wastewater was diluted to an influent nickel concentration of 10 mg/l. The pH of the wastewater was adjusted to 7 by adding 0.1N HCl or 0.1 N NaOH. The relationships between nickel removal percentage and flow rate are shown in Figure 5. Removal percentage of 86.27%, 84.92%, and 75.80% were obtained for the flow rate 5, 10 and 15 liter per day, respectively.

The nickel removal percentage for the influent flow rate of 5 liter per day was the highest among three flow rates tested. This is because smaller flow rate provides longer contact time between wastewater and HFO. In comparison, the difference of 1.6%, nickel removal percentage 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 real application of wastewater treatment.

Effect of feed nickel concentration on column performance

This study was 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. Four nickel concentrations in wastewater were tested: 10, 20, 50, and 100 mg/L. The results obtained in this study are shown in Figure 6. This figure shows that the highest nickel removal percentage, close to 100%, took place at the influent nickel concentration of 10 mg/L in the initial period. 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 removal percentage 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.

Calculation was conducted to determine the nickel accumulated (milligram/gram of iron) at four different influent nickel concentrations, 10, 20, 50, and 100 mg/L. The results are shown in Figure 7. 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 Fe, respectively. These results show that an increase in influent nickel concentration had tendency to increase more nickel sorption capacity. However, column clogging occurred after 55 days of the operation at influent Ni concentration 50 mg/l and after 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 could be adsorbed.

X – Ray Diffraction (XRD)

The initial condition of iron scrap's surface was analyzed with an X – Ray Diffraction Spectrometer. An increase in the signal intensities supports that nickel could be adsorbed with HFO on the surface of iron scrap. The possible structure of the complex might be $NiFe_2O_4$ together with NiO.

CONCLUSIONS

From experimental results, the following conclusions can be drawn:

1. The pH of the wastewater could affect nickel removal efficiency. At neutral and slightly alkaline pH range, nickel ions could be adsorbed to the oxide surfaces, whereas at acidic pH range, the reactions were reversed (desorption) and nickels are released from hydrous ferric oxide. Therefore, it is recommended that the removal of nickel with iron oxide. The pH should be maintained in neutral or slightly alkaline range.

2. Controlling factors for the column studies were contact time, influent nickel concentration and sufficient amount of oxygen. In order to remove nickel efficiently by this process, these factors should be simultaneously compromised.

3. X-Ray Diffraction results supported the findings that nickel can be adsorbed by hydrous ferric oxide on the surface of iron scrap. The structure may be $NiO\text{-}NiFe_2O_4$.

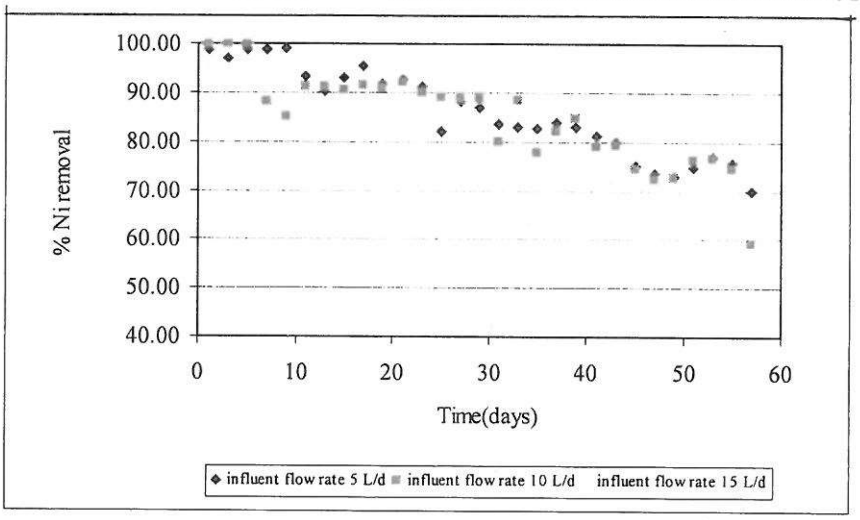

Figure 5 Effect of influent flow rate on Ni removal efficiency

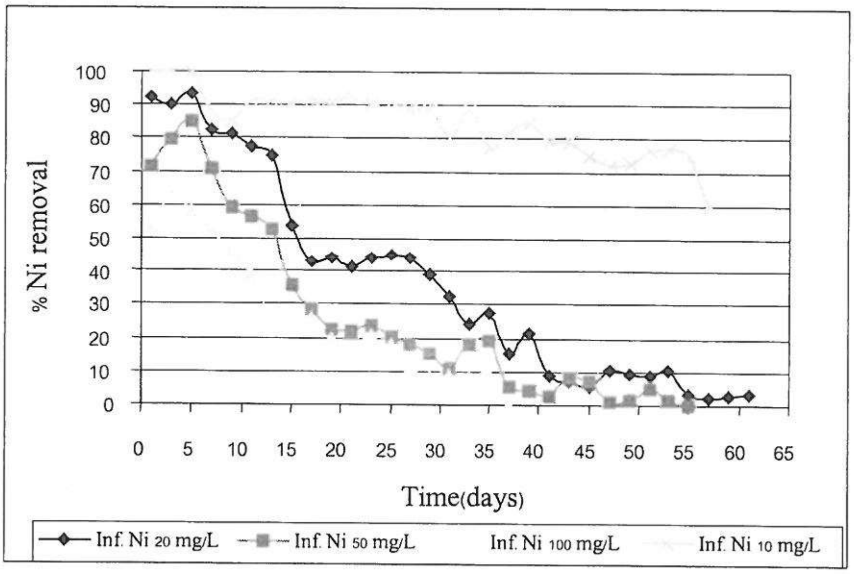

Figure 6 Effect of nickel concentration on column performance

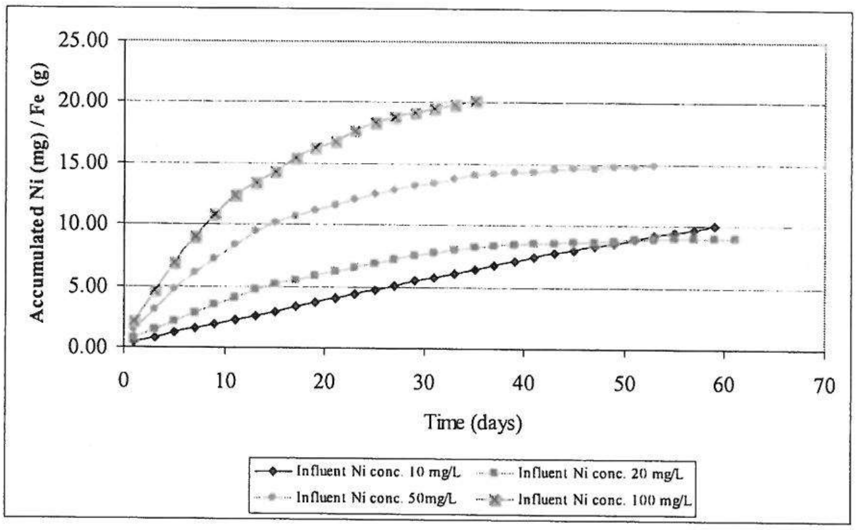

Figure 7 Effect of nickel concentration on HFO's sorption capacity

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