

UPTAKE OF NICKEL(II) USING DIMETHYLGLOXYME CHELATE ANION EXCHANGE RESIN

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ABSTRACT—Uptake of nickel(II) ions from solution are studied using strong base anion resin (*Lewatit M500*, counter ions of Cl⁻) and dimethylglyoxime (*2,3-butanedione dioxime*, H₂DMG) as chelating agent. This study was conducted to determine optimum condition of chelate resin preparation for uptake of nickel(II) ions from solution. The research used batch and column techniques. Batch technique was used to determine the best contact time at chelate resin preparation, capacity of chelate resin (mg Ni²⁺/g), effect of pH stripping (pH 1-5) and pH of nickel(II) solution (pH 4-10) to capacity of chelate resin as well as effect of pH backwash (pH 1-5) to percentage of nickel(II) ions recovery. Column technique was used for uptake of nickel(II) ions from waste water of industrial of metal veneering. Column flow rate was kept constant at 2 mL/minute. Nickel(II) ions which were not removed by chelate resin was quantitatively analyzed with atomic absorption spectrophotometer at wavelength of 232,00 nm. Result of the research revealed the best contact time at chelate resin preparation was 120 - 240 minutes for variation of contact time from 0 to 240 minutes to each 25 gram strong base anion resin. Capacity of chelate resin was obtained about 0,209 to 0,214 mg Ni²⁺/g chelate resin. Capacity of chelate resin decreased progressively after process of stripping that was 0,217 - 0 mg Ni²⁺/g from pH of 5 to 1. The best range pH of nickel(II) solution was obtained at pH of 6 to 7 with capacity of chelate resin from 0,239 to 0,241 mg Ni²⁺/g and selected at pH 6. Percentage recovery of nickel(II) ions increased 21,966 to 75,314% from pH backwash of 5 to 1. With column technique, chelate resin capacity was obtained 0,208 mg Ni²⁺/g and breakthrough point was reached when flow times reached in 60 to 80 minutes.

Keywords: Chelate agent, nickel (II), dimethylglyoxime, strong base anion resin.

INTRODUCTION

Accumulation of heavy metals coming from industrial wastes potentially contribute to water pollution, one of them is electroplating (metal veneering) wastes that generally consist of nickel, copper, zinc and chromium (Elshazly, 2003). At electroplating industry, nickel is applied as protection layer for alloy products (Cotton, 1987). Nickel gives specific biochemical response to human beings at lowest level of 12 µg/kg due to its carcinogenic properties (Stoeppler, 1992). While for potable water the maximum concentration of nickel is 70 mg/L (Fawell, 2005).

The techniques applied to remove nickel from aqueous phase are gravimetric method (Christian, 1986 and Vogel, 1990), adsorption and ion exchangers (Randall, 1992). In gravimetric method dimethylglyoxime (*2,3-butanedione dioxime*, H₂DMG) as a precipitant is used to precipitate nickel forming the red chelate complex, then the precipitate is separated by filtration (Christian, 1986). For trace amount of nickel, gravimetric method is not adequate; therefore adsorption and ion

exchange methods are much applied for nickel at trace level. A research done by Randall (1992) concluded that nickel at trace level could be lowered using biosorbent of chitosan. Ion exchange method is often used for removal nickel at industrial wastes, since the resin can be regenerated and recovered by backwash process (Dofner, 1991).

Nickel(II) can be recovered by cation resin (Elshazly, 2003) or strong base anion resin (Christian, 1986). Cation exchanger resin involves the exchange of nickel(II) ion with counter ion of hydrogen from the resin (Elshazly, 2003). Nickel(II) forms cation complex of [NiCl]⁺ while other cation metals will form anion complexes when strong base anion resin column is eluted with hydrochloric acid 9 M. Only do anion complexes retain at the resin (Christian, 1986).

Removal of metal ions also can be done using chelate resin forming chelate complex compounds with specific metal ion, so that the selectivity of the metal removals increases (Dofner, 1991). Maldovan and Neagu (2002) had recovered iron(III) ion at trace level using chelate resin from strong

base anion resin (counter ion of Cl⁻) and ferron (7-iodo-8-hydroxyquinoline-5-sulphuric acid) as the chelate.

Further, dimethylglyoxime is selective chelate substance for nickel(II) ion (Kolthoff, 1969). The equilibrium of H₂DMG will be shifted to be dimethylglyoxime ion, HDMG⁻, at alkaline solution releasing H⁺ ion. While, counter ion of Cl⁻ from strong base anion resin can be exchanged by dimethylglyoxime anion. Therefore the experiment proposed here, an attempt has been done to study the anion resin with counter ion of HDMG⁻ for removal of nickel(II) in electroplating waste.

MATERIALS AND METHODS

Apparatus – Chromatography column (d: 2 cm and l: 50 cm), magnetic stirrer, analytical balance (Mettler AT 200), pH meter (Hach EC20), AAS PE 3110 and laboratory glassware.

Reagents - NiCl₂.6H₂O, dimethylglyoxime, HCl and NH₃. All chemical used were of analytical reagent grade. The others were strong base anion resin (*Lewatit M500*, Bayer), ethanol 95% and electroplating waste containing copper(II), nickel(II), zinc(II), chromium(VI) taken from Nugroho electroplating, Pati Central Java.

Methods

1. The effect of time for preparation of dimethylglyoxime chelate resin to the uptake of nickel(II) ion

A known amount (25 g) of anion resin was taken in beaker glass containing dimethylglyoxime 1% (100 mL) and NH₃ 25% (1 mL). The mixture was stirred with magnetic stirrer for 60 minutes. Then, it was filtered, washed with water and dried for 5 days at room temperature. The same procedure was applied for resin preparation time of 120, 180 and 240 minutes. To know the effectiveness of each resin prepared was done contacting the resin with 250 mg/L of nickel(II) ions (25 mL) for 60 minutes. Then the filtrate was analysis with AAS.

2. The effect of nickel(II) ion concentration to the chelate resin capacity

The resin (1g) was taken in different beaker glass containing 25 mL of nickel(II) ion with concentration of 6 mg/L. The mixtures were stirred for 6 minutes, filtered and each filtrate

was analyzed by AAS. The procedure was also used for other nickel(II) concentrations (8, 10, 12 and 14 mg/L).

3. The effect of pH stripping to the resin capacity for uptake of nickel(II) ion

The resin (1 g) were taken in different beaker glasses containing 50 mL of nickel(II) ion solutions (5 mg/L) with different acidity (pH of 4,5, 6, 7, 8, 9 and 10). They were stirred for 60 minutes, filtered and each of the filtrates was analyzed with AAS.

4. The effect of pH to the resin capacity for uptake of nickel(II) ion

Chelate resin (1 g) was taken in beaker glass containing 50 mL of nickel(II) ion (5 mg/L) at pH of 4. Then the mixture was stirred for 60 minutes, filtered and the supernatant was analyzed with AAS. The procedure was repeated for different pH of nickel(II) ion solution (pH of 5, 6, 7, 8, 9 and 10).

5. The effect of pH of resin backwash to the recovery of nickel(II) ion

In different beaker glasses containing 50 mL of nickel(II) ion (5 mg/L, at certain pH) solutions were soaked with the resin (1 g) and stirred for 60 minutes . The resins were separated and then they were contacted with 50 mL of HCl (pH of 1, 2, 3, 4 and 5). After being stirred for 5 minutes they were filtered and each of the supernatant was analyzed with AAS.

6. The resin application using column technique to remove nickel(II) from electroplating (metal veneering) wastes

Slurry of chelate resin (5 g) was prepared from the resin mixed with certain amount of water (50 mL). The slurry was poured in chromatography column. The flow rate was kept constant (2 mL/minute) then the waste sample (after dilution) at certain pH was eluted into the column. The effluent was taken for certain times (0, 20, 40, 60, 80, 100, 120, 140, 150, and 170 minutes) in separated bottles and each of which was analyzed with AAS.

RESULTS AND DISCUSSION

The effect of time preparation of dimethylglyoxime chelate resin to the uptake of nickel(II) ion (figure 1) shows that the longer the time for preparation of chelate resin the better the resin to remove nickel(II) ion. There is a sharp increase of the removal

for the resin prepared from 0 to 60 minutes. After the preparation of 60 to 120 minutes the removal of nickel(II) ion is slightly increase. A constant removal of nickel(II) ion is reached at the resin preparation of 120 to 240 minutes. The last resin time preparation was then chosen for the next experiments.

The effect of nickel(II) ion concentration to the chelate resin capacity (figure 2) shows that there is a sharp increase of nickel(II) removal by the resin from nickel(II) concentrations of 6 to 10 mg/L. The concentration beyond 10 mg/L gives a constant removal capacity of nickel(II) ion around 0.209-0.214 mg Ni²⁺/g of the resin.

The effect of pH stripping to the resin capacity for uptake of nickel(II) ion as shown in figure 3 there is a sharp increase at pH of 1-2 and the removal almost constant at pH of 2 until 5. It is due to the fact that the stronger acidity of the solution will increase concentration of chloride ion in the solution, therefore there will be an exchange between counter ions of HDMG⁻ of the resin with chloride anion in the solution, as a result decreasing of the resin capacity. Besides, the sharp decrease of the resin capacity can also be affected by the hydrolysis of chelate resin with increasing acidity. As shown in figure 1, the chelate resin capacity is almost zero at pH stripping of 1 this means that the resin has been completely hydrolyzed.

The effect of pH to the resin capacity for uptake of nickel(II) ion is shown in figure 4. It is seen there is a sharp increase of chelate resin capacity at pH from 4 to 6, and the constant capacity of that is reached at pH between 6 and 9. Finally the resin capacity is slightly decreased at pH from 9 to 10. Formation of insoluble nickel(II) hydroxide was avoided by the use of low concentration of nickel(II) (5 mg/L) and for other experiments the pH was kept constant at 6.

The effect of pH of the resin backwash to the recovery of nickel(II) ion can be seen in figure 5 and table 1. The figure shown that the percentage of nickel(II) recovery increases with the decrease of pH backwash. Friest and Gestrost (1975) conveyed that the complex of nickel(II)dimethylglyoxime is soluble in mineral acids due to hydrolysis of the

complex. Therefore it causes the increase of recovery percentage at lower pH. But lower pH can also lyse the chelate resin into its components.

The resin application using column technique to remove nickel(II) ion from electroplating (metal veneering) wastes is depicted in figure 6. From the figure shows there is an increase of nickel(II) effluent concentration with time of flow rate. Within 0 until 60 minutes the resin can remove all nickel(II) ion, therefore at that time the effluent are free of nickel(II) ion. And the column begins to be saturated at times between 60 and 80 minutes. Saturation is complete after 140 minutes.

CONCLUSION

Chelate resin prepared at time contact within 120-140 minutes gives the best result and the resin capacity that can exchange nickel(II) ion around 0.209-0.214 mg Ni²⁺/g of the resin. The nickel(II) removal from solution was done at pH of 6 and the recovery was occurred at pH of 1.

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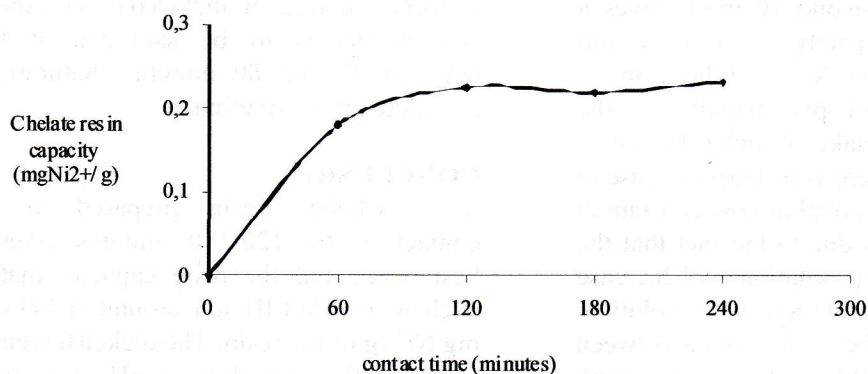


Figure 1.

The effect of time for preparation of dimethylglyoxime chelate resin to the uptake of nickel(II) ion.

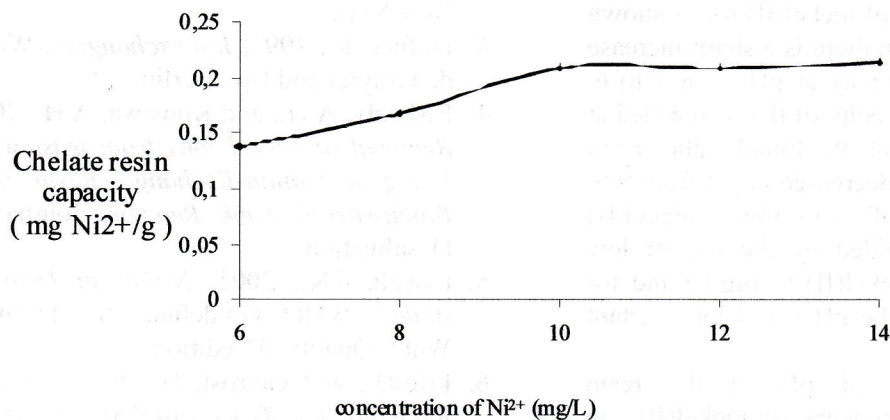


Figure 2.

The effect of concentration nickel(II) ion to the chelate resin capacity

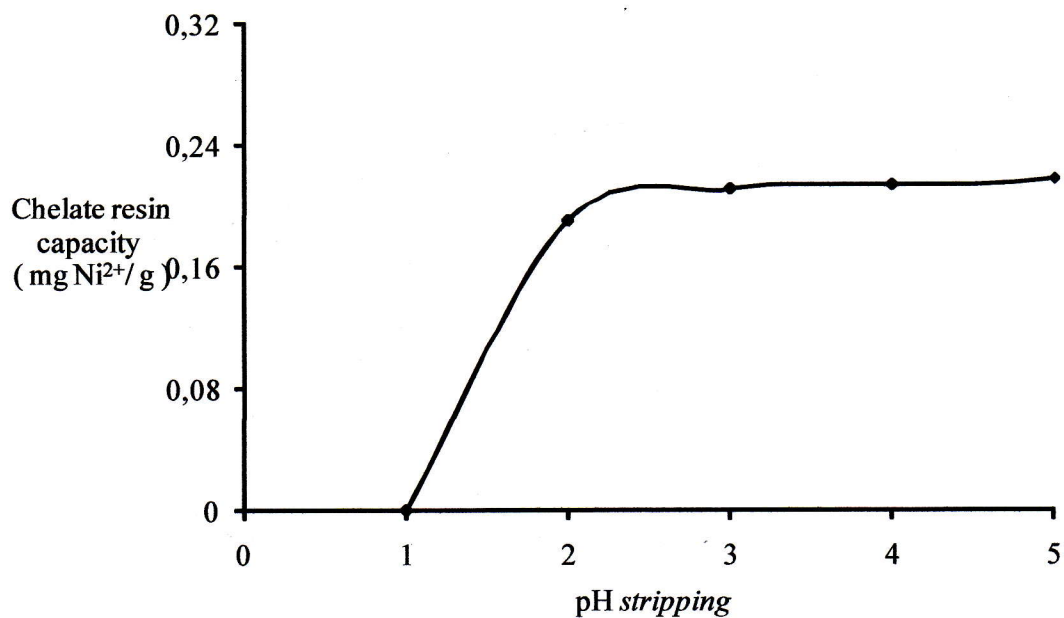


Figure 3.
The effect of pH stripping to the resin capacity for uptake of nickel(II) ion..

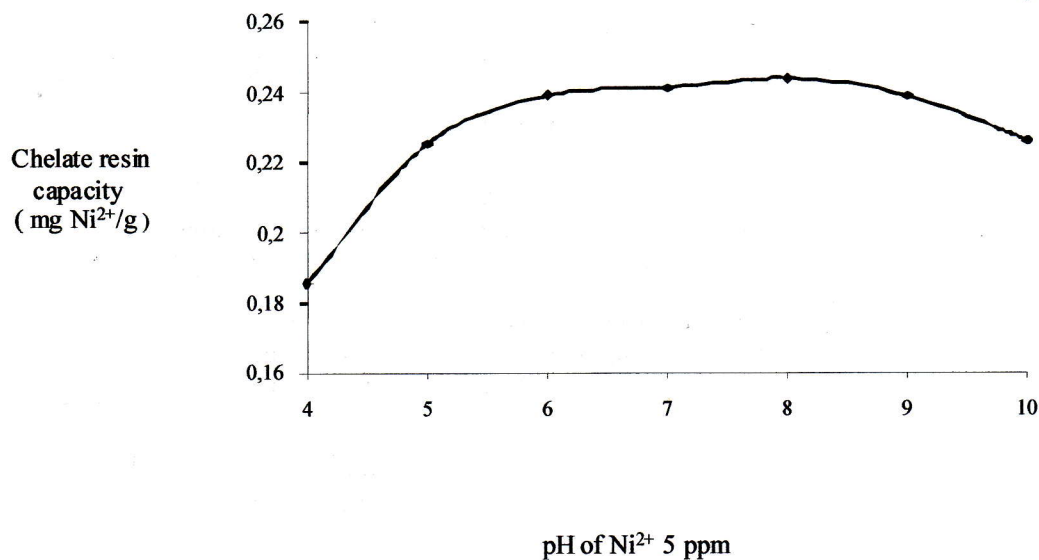


Figure 4.
The effect of pH to the resin capacity for uptake of nickel(II) ion.

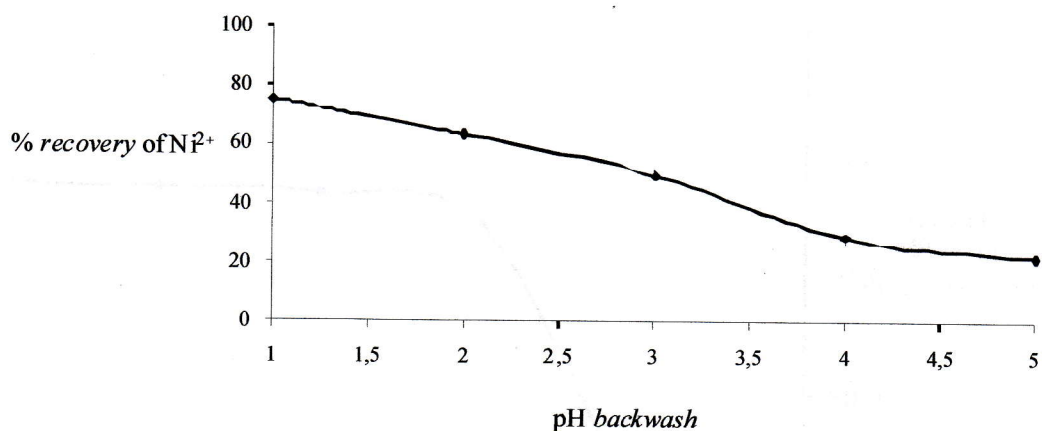


Figure 5.
The effect of pH of the resin backwash to the recovery of nickel(II) ion.

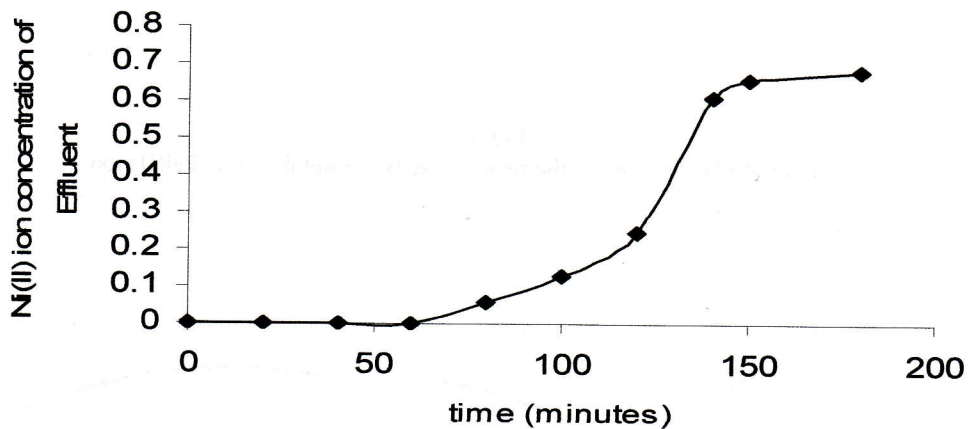


Figure 6.
The resin application using column technique to remove nickel(II) ion from electroplating (metalveneering) wastes (flow rate of 2 mL/minute).

Tabel 1. The resin application using column technique to remove nickel(II) ion from electroplating (metal veneering) wastes (flow rate of 2 mL/minute)

Time (minutes)	Ni(II) concentration of Effluent
0	0
20	0
40	0
60	0
80	0.06
100	0.13
120	0.25
140	0.61
150	0.66
180	0.68