Recovery of metallic nickel from waste sludge produced by electrocoagulation of nickel bearing electroplating effluents

K.I. Dermentzis[*,1,2], D.I. Marmanis[1], A.K. Christoforidis[1,2], N.C. Kokkinos[1,2], D.K. Stergiopoulos[1]

[1]Department of Petroleum and Mechanical Engineering, Eastern Macedonia and Thrace Institute of Technology, Kavala, Agios Loukas, 65404, Greece
[2]Hephaestus Advanced Research Laboratory, Eastern Macedonia and Thrace Institute of Technology, Kavala, Agios Loukas, 65404, Greece
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[*]Presenting author email: demerz@otenet.gr

Abstract
The conventional techniques used to remove toxic metals from industrial effluents are carried out by precipitation with a base or sulfide, coagulation with inorganic or organic coagulants and electrocoagulation with aluminum or iron anodes. These techniques produce a hazardous sludge very rich in heavy metals.
The present work proposes an integrated process to recover pure metallic nickel from industrial galvanic nickel waste. The process involves three subsequent steps: A) Treatment of nickel bearing electroplating effluents by electrocoagulation with aluminum electrodes and production of a sludge containing mainly $Ni(OH)_2$ and $Al(OH)_3$. B) Acid digestion of the sludge followed by controlled pH increase to preferentially separate the $Al(OH)_3$. C) Recovery of pure metallic nickel by electrowinning.
The initial Ni^{2+} ion concentration of 95 mg/L in effluent was successfully reduced under the permissible limits (<2 mg/L). The sludge was then treated with H_2SO_4 and NaOH for digestion, precipitation and separation of $Al(OH)_3$, while Ni^{2+} ions remain in solution. Electrowinning of the obtained concentrated solution containing 1000 mg/L Ni^{2+} ions produced pure metallic nickel by electrodeposition on the copper cathodes.
The proposed technology offers relevant metal companies the opportunity for significant cost benefit through metal recovery from industrial waste which would otherwise result in landfill.

Introduction

Many industries produce significant quantities of solid or liquid industrial waste containing heavy metals without recovery of valuable materials from the waste streams. Industrial effluents from nickel electroplating industries contain high amounts of nickel ions, which are of considerable concern because they are non-biodegradable and highly toxic. Only 30-40% of the metal used in plating processes is effectively utilized i.e. plated on the articles. The rest contaminates the rinse waters during the plating process when the plated objects are rinsed upon removal from the plating bath. Waste streams from nickel electroplating industries may contain up to 500 ppm Ni^{2+} ions. The conventional techniques used to remove toxic metals from industrial effluents are carried out by precipitation with a base or sulfide, coagulation with inorganic or organic coagulants and electrocoagulation with electrodissolution of soluble aluminum or iron anodes [1,2]. These techniques produce a sludge which is very rich in heavy metals, is considered highly toxic and hazardous and, therefore, must be disposed of using special facilities at great expenses to industry [3]. From the viewpoint of environmental protection and resource saving, effective recycling and reusing of the heavy metal containing waste is strongly expected.

Several treatment processes have been suggested for the removal of nickel ions from aqueous waste streams: adsorption [4], biosorption [5], ion exchange [6], chemical precipitation [7] and electrochemical methods: electrowinning [8], electrodialysis [9], electrodeionization [10], membrane-less electrostatic shielding based electrodialysis/electrodeionization [11] and electrocoagulation.

Hydroxide precipitation is the most common conventional treatment applied to the metal plating wastewaters to remove heavy metals. The method is based on low solubility of metal hydroxides at alkaline pH values. As the metals are converted to metal hydroxide solid phase they are separated from wastewater by physical means such as sedimentation, flotation and filtration. Hydroxide precipitation performance on free metal removal is perfect at the optimum pH where metal solubility is the lowest. The optimum pH value for nickel is 10.2. The obtained nickel solubility at this optimum pH is about 0.001 mg/L. Sulphide precipitation based on low solubility of metal sulfides is also applied to metal bearing wastewaters to remove heavy metals. This method is very efficient in free and particularly complexed metals [12]. The amount of sludge produced by sulphide precipitation is higher than that

produced by hydroxide precipitation. Handling and disposal of the sludge produced by sulphide precipitation is difficult due to its hazardous nature.

The solid phases initially formed may be very finally divided during hydroxide precipitation and hard to separate by gravity. Sodium hydroxide using pH adjustment generally causes to form smaller particles but upon coagulation they yield a very clear supernatant. The best solution to solid formation and separation problem is the use of inorganic and organic coagulants. For this purpose, $FeCl_3$, alum, and various polyelectrolytes are commonly used as coagulant aid agents in the hydroxide precipitation application.

The amounts of the precipitated sludge containing the concentrated nickel hydroxides or sulfides is an extremely hazardous waste and must be disposed of using special facilities at great expense to industry. From the viewpoint of environmental protection and resource saving, effective recycling and reusing of the nickel containing wastewater is strongly expected. Closed-recycle system or so-called effluent-free technology should be developed.

Electrocoagulation uses no chemicals as coagulating agents. These are generated during the electrolysis process by electrodissolution of a sacrificial anode made of aluminium or iron. Electrocoagulation has been successfully performed for treatment and remediation of textile wastewaters [13], oil wastes [14], diary effluents [15], diesel and biodiesel wastewaters [16], laundry wastewaters [17], slaughter house effluents [18], arsenic or fluoride containing waters [19,20] and heavy metal bearing effluents [21,22].

The present work proposes an integrated process to recover pure metallic nickel from industrial galvanic nickel containing waste. The process involves three subsequent steps: a) Treatment of nickel bearing electroplating effluents by electrocoagulation with aluminum electrodes and production of a sludge containing mainly $Ni(OH)_2$ and $Al(OH)_3$ and some organic contents. b) Acid digestion of the sludge at 50 ^0C followed by controlled pH increase to preferentially precipitate and separate the aluminum hydroxide. The aluminum hydroxide solid can be then filtered out producing a concentrated nickel solution with low aluminum content, suitable for electrowinning. C) Recovery of pure metallic nickel by electrowinning.

Metal processing and finishing companies are under extreme financial and environmental pressure, due to increasing cost of metals, cost of waste disposal and environmental impact. The proposed technology offers relevant metal companies the opportunity for significant cost benefit through metal recovery from industrial waste which would otherwise result in landfill.

1. Materials and Methods
1.1 Chemicals

H_2SO_4, NaOH, KCl, $(NH4)_2SO_4$ and NH_3 were of analytical grade (Merck). The value of pH was adjusted by 0.1 M solutions of H_2SO_4 and NaOH as required. The actual wastewater was obtained from an electroplating unit located near Thessaloniki, northern Greece. Its main characteristics are listed in Table 1.

Table 1. Main characteristics of the electroplating wastewater sample

Parameter:	Value:
pH	6.3
Conductivity (µS/cm)	1200
COD (mg/L)	315
Ni^{2+} (mg/L)	95
Cl- (mg/L)	22
SO_4^{2-} (mg/L)	146

1.2 Apparatus

A laboratory model DC power supply apparatus (PHYWE, STELL TRAFO, PHYWE Systeme GmbH & Co. KG. Germany) was used to maintain constant DC current. Voltage and current were measured by a multimeter (PHYWE). Conductivity was measured by means of a conductometer (inoLab Cond. Level 1, WTW). The pH and the temperature were measured using a Hanna (HI8314) pH-meter.

250 mL of the treated wastewater was placed in a 500 mL cylindrical glass vessel serving as the electrocoagulation and electrowinning reactor. The electrodes for electrocoagulation were three symmetrical cylindrical aluminum plates (the two outer plates used as cathodes and the middle one as anode), while for electrowinning two outer copper plates served as cathodes and the middle platinized titanium plate (Ti/Pt) as anode. All electrodes had the same dimensions of 10 x 5x 0.2 cm and were

submerged to 6 cm in the treated solution with a total effective area of 60 cm^2 for both, anode and cathode. The interelectrode distance was 1.5 cm. To remove the oxide and passivation layer from aluminum surface the electrodes were grinded with sandpaper and activated by dipping them in HCl 5N KCl for 1 minute. 0.5 g KCl was added to every treated solution. The added KCl serves for prevention of passivation on the aluminium electrode surface and decrease of the excessive ohmic drop in the solution. Samples were extracted every 5 minutes, filtered using Whatman filter paper (Grade 40) and brought to analysis.

The actual nickel effluent containing 95 mg/L Ni^{2+} ions was obtained from an electroplating unit near Thessaloniki, northern Greece. The effluent was treated by electrocoagulation at various current densities 10, 20 and 30 mA/cm^2. The Ni^{2+} ion concentration was successfully reduced under the permissible limits for effluent discharge (<2 mg/L). The produced electrocoagulation sludge of $Ni(OH)_2/Al(OH)_3$ was filtered, dried at 80 ^{0}C and weighted. The sludge was then dissolved in H_2SO_4 and subsequently treated with 0.1 M NaOH until pH reached the optimum value of 4.8 for precipitation and separation of $Al(OH)_3$, while Ni^{2+} ions remain in solution. Electrowinning of the concentrated solution containing 1000 mg/L Ni^{2+} ions produced pure metallic nickel by electrodeposition at the copper cathodes.

1.3 Analytical methods

The residual nickel and aluminum concentrations were determined by Atomic Absorption Spectroscopy AAS (Perkin Elmer 5100), whereas the concentrations of Cl$^-$ and SO_4^{2-} ions were measured by UV spectrophotometry (Hitachi 2000). The chemical oxygen demand (COD) was analyzed using a COD reactor (Thermoreaktor TR 420, MERCK) and a direct reading spectrophotometer (Spectroquant Pharo100, MERCK).

2. Results and Discussion
2.1 Treatment of nickel bearing electroplating effluents by electrocoagulation

Electrocoagulation is a process consisting of creating metallic hydroxide flocks inside the wastewater by electrodissolution of soluble anodes made of aluminium or iron. The main reactions occurring during electrocoagulation with aluminum electrodes produce aluminum ions at the sacrificial anode and hydroxide ions as well hydrogen gas at the cathode:

$$Al \rightarrow Al^{3+} + 3e^- \qquad \text{(anode)}$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad \text{(cathode)}$$
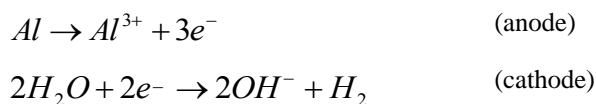
The generated Al^{3+} and OH$^-$ ions react to form various monomeric and polymeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)^{4+}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{7+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$ which finally result in situ formation of gelatinous $Al(OH)_3$ effecting the coagulation and co-precipitation or H_2 flotation of particulates from the solution by adsorption [13]. The aluminum hydroxide flocks act as absorbents for heavy metal ions. Furthermore, heavy metal ions combine with the electro-generated OH$^-$ ions at the cathode and precipitate in form of their insoluble hydroxides. Both phenomena act synergistically leading to a rapid removal of heavy metal pollutants from water.

According to literature, the solution pH has a considerable effect on the efficiency of the electrocoagulation process. In addition, pH changes during the process dependent on the anode material and the initial pH value of the treated solution. Vik *et al.* [23] reported that the observed increase of pH at low initial pH (<7) is ascribed to the hydrogen evolution and the generation of OH$^-$ ions at the cathodes. In alkaline medium (pH>8) the final pH does not change markedly because the generated OH$^-$ ions at the cathodes are consumed by the generated Al^{3+} ions at the anode forming the needed $Al(OH)_3$ flocks. Furthermore, OH$^-$ ions can also partially combine with the Ni^{2+} ions to form the insoluble hydroxide precipitate $Ni(OH)_2$.

Experiments were conducted using the Ni^{2+} ion bearing wastewater of 95 mg/L in the initial pH range 2-10. As can be obtained from Table 2 the removal efficiency of Ni^{2+} ions after 30 minutes of electrolysis time at the constant current density of 20 mA/cm^2 reached very high values (>97%) in the pH range 4-10. The removal percent is very low at pH=2. It increases considerably at pH=4, remains high and almost constant in the pH range 4-10 and slightly decreases at pH>10. In alkaline medium (pH>8) the removal of Ni^{2+} ions, beyond electrocoagulation, can also occur partially by precipitation as insoluble nickel hydroxide, $Ni(OH)_2$ as already stated. The appropriate pH range for effluent discharge is 5.5 - 9. Furthermore, the increased solubility of $Al(OH)_3$ in alkaline solutions may lead to increased

Al concentration in the treated electrocoagulation effluent above the environmental standards. Therefore, it is better to carry out the electrocoagulation process in this appropriate pH range.

Table 2. Removal percentage of nickel at various initial solution pH values

Initial pH :	Removal %:
2	27.8
3	83.2
4	96.6
5	98.5
6	98.7
7	98.2
8	99.2
9	99.2
10	99.1

It is well known that the applied current density determines the coagulant dosage rate, the bubble production rate and size and the flock growth. Adhoum et al. [24] and Colder et al. [25] used current densities between 8 and 48 mA/cm^2 and demonstrated that the increase of applied current density enhanced the treatment rate resulting in a faster removal of pollutants. Table 3 shows the effect of applied current density on the removal rate of nickel versus time of electrolysis.

Measurements were carried out at different current densities 5-20 mA/cm^2 using the nickel contaning wastewater of 95 mg/L Ni^{2+} and not adjusted initial solution pH 6.3. According to Table 3 the removal rate of nickel increased, as expected, with increasing current density. In only 20, 30 and 40 minutes of electrolysis time at the corresponding current densities 20, 10 and 5 mA/cm^2 nickel ions have been almost quantitatively removed (>99%) and their residual concentration fell under the admissible limits (2 mg/lit) for effluents discharge to sewage systems. The pH value decreased slightly to around 5 during the first stage of the electrocoagulation treatment and increased afterwards to a final constant value of around 8. The concentration of Al^{3+} ions in the treated solution after the electrocoagulation treatment at the three applied current densities 5, 10 and 20 mA/cm^2 amounted to 342, 356 and 364 μg/L which are in the appropriate range for aluminum containing effluent discharge to sewage systems.

Table 3. Removal percentage of nickel with time and various applied current densities

Time (min)	(5 mA/cm^2)		(10 mA/cm^2)		(20 mA/cm^2)	
	Residual Ni^{2+} Concentration (mg/L)	Removal efficiency (%)	Residual Ni^{2+} Concentration (mg/L)	Removal efficiency (%)	Residual Ni^{2+} Concentration (mg/L)	Removal efficiency (%)
0	95.0	-	95.0	-	95.0	-
10	60.5	36.3	41.2	56.6	28.3	70.2
20	34.2	64.0	11.6	87.7	0.8	99.2
30	15.5	83.6	0.9	99.1		
40	1.2	99.0				

Organic compounds contained in the treated wastewater sample also compete for absorption on the Al(OH)$_3$ flocks. As known, various organics are added to the electroplating baths, such as complex former, brighteners, buffering and wetting agents. At the same time, the COD of the wastewater also decreased from the initial value of 315 mg/L to 106 mg/L after 30 min of electrocoagulation time at the applied current density of 20 mA/cm^2, which corresponds to a removal efficiency of about 66.3 %. It reached then a plateau and remained almost constant at longer electrolysis time (Table 4). Consequently, electrocoagulation is an effective method for removing simultaneously both, heavy metals and organic pollutants from wastewater.

**Table 4**. Reduction of wastewater COD with electrocoagulation time

Time (min)	COD (mg/L)
0	315
10	196
20	125
30	106
40	105
50	105

2.2 Sludge leaching and separation of nickel from aluminum

The precipitated sludge was collected, dried at 80 °C for 24 h, cooled in a desiccator and weighed. It consists mainly of nickel in form of $Ni(OH)_2$ and aluminum in form of $Al(OH)_3$ and additionally of some absorbed organics originated from the organic additives contained in the treated actual electroplating wastewater. The amount of the produced sludge is based on the Faraday's law. The electrocoagulation treatment produces less sludge compared to that produced by the conventional chemical coagulation process.

A fixed amount of 10 g dried sludge was leached with 1000 ml H_2SO_4 of different concentrations in stirring conditions of 200 rpm and different constant temperatures (Table 5). The nickel and aluminum extraction occurred in only a few minutes of leaching time and amounted to 98 and 92 % respectively. The solid residue was separated from solution by centrifugation, washed with distilled water, dried at 103 °C for 24 h and chemically analyzed. The solid residue contains <0.6 % nickel and can be disposed of in an appropriate landfill. According to Table 5, the obvious difference between the initial and final pH is indicative of the H_2SO_4 acid consumption needed for digestion of the treated sludge. The acid consumption was found to range between 0.6 and 0.9 kg of H_2SO_4 per kg of sludge.

Considering that in the sludge the metals occur as hydroxides, the stoichiometric reactions during leaching are:

$$Ni(OH)_2 + H_2SO_4 \rightarrow NiSO_4 + 2H_2O$$

$$2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O$$
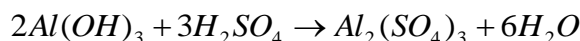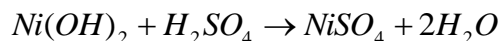
Table 5. Leaching results of electrocoagulation sludge at various temperatures and pHs values

Temperature (°C)	[H_2SO_4] (M)	pH initial	pH final
25	0.05	1.25	2.12
	0.1	0.99	1.51
	0.2	0.68	0,98
50	0.05	1.15	2.22
	0.1	0.95	1.58
	0.2	0.61	1.04
75	0.05	1.10	2.23
	0.1	0.88	1.65
	0.2	0.95	1.12

2.3 Separation of Ni^{2+} from Al^{3+} ions

The separation of Ni^{2+} from Al^{3+} ions can occur under controlled pH, due to the different solubility of their hydroxides. The solubility product of $Al(OH)_3$ is 1.99×10^{-33} and of $Ni(OH)_2$ 1.58×10^{-14}. According to Jander and Blasius [26] from an initial solution of 10^{-2} M of both metals, precipitation of insoluble $Al(OH)_3$ begins at pH=3.8 and ends at pH= 4.8, while precipitation of insoluble $Ni(OH)_2$ begins at pH=8.1 and ends at pH= 9.6 respectively. Therefore, after the acid digestion and solubilization of the produced $Al(OH)_3/Ni(OH)_2$ electrocoagulation sludge, the solution pH is

increased, under control, by addition of appropriate amount of 0.1 M NaOH solution until it reaches pH=4.8. At this pH value aluminum is almost quantitatively precipitated in form of $Al(OH)_3$, while Ni^{2+} ions remain in solution. The $Al(OH)_3$ solids are filtered out and concentrated Ni^{2+} solutions of 1 to 10 g/L can be obtained appropriate for metallic nickel electrowinning.

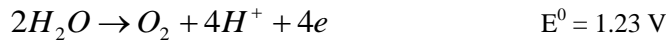### *2.4 Recovery of metallic nickel by electrowinning*

The electrodeposition of metallic nickel can occur from both, acidic and alkaline solutions. Hydrogen evolution is a side reaction and aimless energy consumption. Therefore, it should be avoided. The production of hydrogen increases with decreased nickel concentration and decreased pH.

The main reactions from acidic sulfate solutions are:
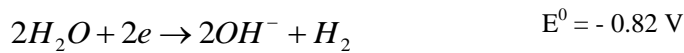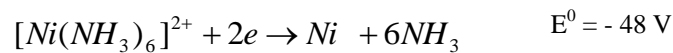
Cathodic reactions:

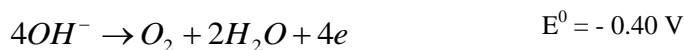$$Ni^{2+} + 2e \rightarrow Ni \qquad\qquad E^0 = - 0.27 \text{ V}$$

$$2H^+ + 2e \rightarrow H_2 \qquad\qquad E^0 = 0.00 \text{ V}$$

Anodic reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \qquad\qquad E^0 = 1.23 \text{ V}$$

The main reactions from alkaline ammoniacal solutions are:

Cathodic reactions:

$$[Ni(NH_3)_6]^{2+} + 2e \rightarrow Ni + 6NH_3 \qquad\qquad E^0 = - 48 \text{ V}$$

$$2H_2O + 2e \rightarrow 2OH^- + H_2 \qquad\qquad E^0 = - 0.82 \text{ V}$$

Anodic reaction:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e \qquad\qquad E^0 = - 0.40 \text{ V}$$

From the reduction potentials of the above reactions can be concluded that the hydrogen evolution is less competitive with nickel electrodeposition in alkaline ammoniacal than in acidic solutions. This effect has been studied by Lupi et al. [27]. To hinder the hydrogen evolution, $(NH_3)_2SO_4$ and NH_3 have been added to the treated solution until it reached an ammoniacal buffer of pH=9.5.

The cylindrical electrowinning reactor was equipped by a thermostatic water jacket connected with thermostatic bath. Electrowinning experiments were conducted at 40 ^{o}C in galvanostatic operations and stirring conditions of 200 rpm. By applying constant current densities of 5, 10 and 20 mA/cm^2, almost quantitative electrodeposition of pure metallic nickel was achieved on the cathodes in 80, 40 and 30 minutes of electrolysis time respectively, leaving a residual solution with Ni^{2+} ion concentration of less than 5 mg/L, as illustrated in Table 6. The concentration of 5 mg/L in this treated solution of small volume can further be decreased to <2 mg/L by pouring the solution into the initial wastewater before the electrocoagulation treatment. It was estimated that about 1.5 Kg of high value metallic nickel could be obtained from 10 Kg of electrocoagulation sludge.

Table 6. Mass of electrodeposited metallic nickel versus electrolysis time at various applied currents

Time (min)	5 mA/cm^2	10 mA/cm^2	20 mA/cm^2
0	1000	1000	1000
10	756	662	512
20	551	314	165
30	362	92	5
40	248	5	
50	105		
60	51		
70	11		
80	4		

2.5 Electrical energy consumption

The electrical energy consumption E for both, electrocoagulation and electrowinning treatment is calculated from following equation:

$$E = \frac{U \cdot I \cdot t}{mNi}$$

where
U = voltage (Volts)
I = current intensity (A)
t = time (h)
mNi = mass of nickel removed from wastewater during electrocoagulation or mass of metallic nickel electrodeposited on the cathode during electrowinning .

The electrical energy consumption at the applied current density of 20 mA/cm^2 for the electrocoagulation treatment of the electroplating wastewater amounts to 13.33 kWh per kg of Ni removed from treated wastewater and for electrowinning to 3.25 kWh per kg of Ni produced at the cathode.

3. Conclusions

Electrocoagulation with aluminium electrodes is a safe and convenient route for effective removal of heavy metals, such as nickel from water and wastewater. Best removal capacity was achieved in the pH range 4-10. Removal rate increased with increasing applied current density. The nickel concentrations in the treated industrial wastewater fell under the admissible limits in only few minutes of electroprocessing. At the same time, dissolved organic compounds present in electroplating wastewater are also removed. In comparison to chemical coagulation, where an increased coagulant dosage and several hours are needed, electrocoagulation is a faster and more economical method for removing metallic and organic pollutants from water and industrial effluents.
After the acid digestion of the electrocoagulation sludge, controlled pH increase to 4.8 and filtration of the precipitated aluminum hydroxide, pure metallic nickel is obtained by electrowinning from the concentrated ammoniacal nickel solution.
The proposed technology yields 1.5 Kg of high value metallic nickel from 10 Kg of electrocoagulation sludge, leaving almost nickel free solid waste and water. The technology offers relevant metal companies the opportunity for significant cost benefit through metal recovery from industrial waste which would otherwise result in landfill.

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