Nickel removal from wastewater by electrocoagulation with aluminum electrodes

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Abstract

In this study, the performance of electrocoagulation with aluminium electrodes for removing nickel from synthetic aqueous solutions and actual electroplating wastewater was investigated. Parameters affecting the electrocoagulation process, such as initial pH, current density, initial metal ion concentration and contact time were investigated. The removal efficiency is very high in the pH range 4-10. Increased current density accelerated the electrocoagulation process, however, on cost of increased energy consumption. Initial Ni^{2+} concentrations of 100-300 mg/lit were quantitatively reduced under the admissible limits in only 10-20 minutes of electrolysis time respectively at the current density of 30 mA/cm^2. The process has proved to be efficient in removing Ni^{2+} ions also from industrial electroplating effluents, where an initial Ni^{2+} concentration of 215 mg/lit fell under the legal limits in 20 minutes.

Keywords: electrocoagulation, electroflotation, sacrificial aluminium anode, electroplating effluent.

1. Introduction

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 are 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. Nickel is a toxic heavy metal and nickel compounds, for instance nickel sulphide, are suspected to cause cancer [1]. Waste streams from nickel electroplating industries may contain up to 500 ppm Ni^{2+} ions, which according to environmental regulations worldwide must be controlled to an acceptable level (<2 ppm) before being discharged to the environment.

Several treatment processes have been suggested for the removal of nickel ions from aqueous waste streams: adsorption [2,3], biosorption [4,5], ion exchange [6], chemical precipitation [7,8] and electrochemical methods: electrowinning [9.10], electrodialysis [11], electrodeionization [12,13], membrane-less electrostatic shielding based electrodialysis/electrodeionization [14-16] 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. On the other hand, metal plating baths are not prepared using only metal salts and the recipe of the metal plating bath generally includes complexing agent, carrier, brightener, one or more than one metal salts and chloride or other salts. The complexing agent is used in the metal plating baths to prevent the metals from being precipitated. In this case, a wastewater containing complexing agents cannot be treated to remove metals by hydroxide precipitation within the limits of usual operation and it requires its modification called as high pH hydroxide precipitation [Tünay and Kabdaşlı (7), Tünay et al.(17)] or another treatment method application such as sulphide precipitation, electrocoagulation etc. 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. 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 are 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 [18,19], oil wastes [20,21], diary effluents [22], diesel and biodiesel wastewaters [23,24], laundry wastewaters [25], slaughter house effluents [26], arsenic or fluoride containing waters [27,28] and heavy metal bearing effluents [29-34].

This paper reports the efficiency of electrocoagulation in removing metallic pollutants, such as nickel ions from synthetic aqueous solutions and actual electroplating wastewater.

2. Materials and Methods

2.1 Chemicals

$NiSO_4 \cdot 7H_2O$, KCl and NaOH were of analytical grade (Merck). pH was adjusted by 0.1 M solutions of HCl 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 actual wastewater sample

pH		6.5
Conductivity (mS/cm)		1.4
COD (mg/L)		324
Ni^{2+} (mg/L)		215
Cl^- (mg/L)		40
SO_4^{2-} (mg/L)		275

2.2 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 connected to a combined electrode comprising a temperature sensor (HI1217D).

Electrolyses were conducted at room temperature in a cylindrical glass cell of 500 ml in which aliquot solutions of 250 ml were placed and slowly stirred with a magnetic bar at 500 rpm. Four commercially obtained aluminium plates of size 10cm x 5cm x 0.5cm immersed to a 5 cm depth with an effective area of 20 cm^2 each, were used as electrodes in the experiments. The electrodes were connected in a monopolar mode with a total anode surface of 60 cm^2. The interelectrode distance was 1.5 cm. To remove the oxide and

passivation layer from aluminium surface the electrodes were grinded with sandpaper and energized 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). The residual nickel and aluminium 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).

At the end of each experiment the produced sludge was measured.

2.3 Brief description of 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 produce aluminium ions at the sacrificial anode and hydroxide ions as well hydrogen gas at the cathode:

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

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad \text{(cathode)}$$
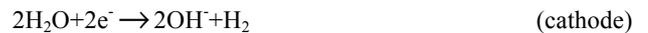
The generated Al^{3+} and OH^- ions react to form various monomeric and polymeric species such as $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)^{4-}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{7+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$ which finally result in situ formation of gelatinous $Al(OH)_3$ effecting the coagulation and co-precipitation or H_2 flotation of particulates from the solution by adsorption [Kobya et al, (18)]. The aluminium 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.

3. Results and Discussion

3.1 Effects of operating parameters

The electrocoagulation process is affected by several operating parameters, such as initial pH, pollutants concentrations, current density and contact time. In the present study all these have been explored in order to evaluate a treatment technology for nickel removal from synthetic solutions and actual electroplating wastewaters.

3.1.1 Initial pH

According to literature, 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.* [35] 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 Ni^{2+} solutions of of 50 mg/lit in the initial pH range 2-10. As can be obtained from Table 2 the removal efficiency of the metal ions after 20 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 heavy metals, beyond electrocoagulation, can also occur partially by precipitation as insoluble hydroxides 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 [36]. Therefore, it is better to carry out the electrocoagulation process in this appropriate pH range.

Table 2. Effect of pH on nickel removal. Initial nickel concentration = 100mg/lit, current density = 20mA/cm^2, electrolysis time = 15 minutes, effective anode surface = 60 cm^2

Initial pH	2	3	4	5	6	7	8	9	10
Removal %	28.1	84.4	97.5	98.4	97.4	98.8	99.6	98.5	99.2

3.1.2 Applied current density

It is well known that the applied current density determines the coagulant dosage rate, the bubble production rate and size and the flock growth [30,37,38]. Adhoum et al. [30] and Colder et al. [39] 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 following parameters, such as the removal rate of nickel, solution pH, amount of generated sludge, electrical energy consumption and concentration of aluminium in the treated solution, versus time of electrolysis.

Measurements were carried out at different current densities 10-30 mA/cm^2, at a constant heavy metal concentration of 250 mg/lit and pH 7.5. According to Table 2 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 30, 20 and 10 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. By doubling the applied current density from 10 to 20 mA/cm^2 the time of electroprocessing decreases from 40 to 30 minutes, but the overal electrical energy consumption increases almost by the factor of 3 i.e. from 3.52 to 10.207 wh/g Ni removed. (Table 3). The pH value decreased slightly to around 5 during the first stage of the electrocoagulation treatment and increased afterwards to around 8.

The aluminium concentration after the electrocoagulation treatment at the three applied current densities 10, 20 and 30 mA/cm^2 amounted to 365, 340 and 355 μg/L which are in the appropriate range for effluent discharge to sewage systems.

Table 3. Effect of current density on removal efficiency of nickel with time. Initial nickel concentration = 250 mg/lit, effective anode surface = 60 cm^2, solution volume = 250 ml.

Current density (mA/cm^2)	Time (min.)	Residual Ni^{2+} Concentration (mg/L)	Removal efficiency (%)	pH	Al consumption (gAl/gNi)	Sludge amount (gTSS/gNi)	Energy consumption (wh/gNi)	Al concentration (μg/L)
	0	250.0		7.5				
10	10	175.5	29.8	5.0				
	30	48.6	80.6	6.8				
	30	48.6	80.6	7.6				
	40	1.9	99.2	8.1	0.655	3.471	3.52	360
	0	250.0		7.5				
20	10	117.6	52.9	5.8				
	20	44.8	82.1	7.7				
	30	0.9	99.6	8.2	0.982	4.422	10.207	365
30	0	250.0		7.5				
	10	74.6	70.1	7.1				
	20	1.9	99.2	8.3	1.229	5.128	20.610	365

3.1.3 Initial metal ion concentration

To demonstrate the effect of initial metallic pollutants concentration and the time required for their quantitative removal, a set of experiments was conducted with different initial concentrations 100, 200 and 300 mg/lit of nickel ions. Each solution was treated at a constant current density of 30 mA/cm^2 and different times of electrolysis.

Table 4 shows the variations of the different concentrations of nickel, the solution pH, the amount of generated sludge, the electrical energy consumption and the effluent aluminium concentration versus the electrolysis time. The residual nickel ion concentrations were reduced to admissible levels after only 10, 15 and 20 minutes respectively. According to Table 3, no direct correlation exists between metal ion concentration and removal efficiency. Certainly, for higher concentrations longer time for removal is needed, but higher initial concentrations were

reduced significantly in relatively less time than lower concentrations. The electrocoagulation process is more effective at the beginning when the concentration is higher than at the end of the operation when the concentration is low.

Also here a slight decrease of pH is observed at the beginning of the electrocoagulation treatment which finally

increases again when nickel ions are almost quantitatively removed from the treated solutions. The aluminium concentration after the electrocoagulation treatment of the three solutions of 100, 200 and 300 mg/L Ni amounted to 340, 350 and 355 μg/L respectively, which are in the appropriate range for effluent discharge to sewage systems.

Table 4. Effect of initial concentration on removal efficiency of nickel ions. Current density = 30 mA/cm^2, effective anode surface = 60 cm^2, solution volume = 250 ml.

Initial Ni^{2+} concentration (mg/lit)	Time (min.)	Residual Ni^{2+} concentration (mg/lit)	Removal efficiency (%)	pH	Al consumption (gAl/gNi)	Sludge amount (gTSS/gNi)	Energy consumption (wh/gNi)	Al concentration (μg/L)
100	0	100.0		7.5				
	5	44.3	55.7	6.0				
	10	0.9	99.1	7.2	1.228	5.140	20.850	340
200	0	200.0		7.5				
	5	134.8	32.6	4.9				
	10	38.9	80.5	6.1				
	15	0.8	99.6	7.8	0.921	4.733	15.547	350
300	0	300.0		7.5				
	5	230.8	23.1	4.6				
	10	141.4	52.8	5.8				
	15	51.2	82.9	6.6				
	20	1.2	99.6	7.4	0.818	3.942	13.641	345

3.2 Treatment of actual wastewaters

The applicability of the electrocoagulation process for actual wastewater was validated by treating a sample of industrial effluent, collected from an electroplating unit (Table 1). The residual nickel concentration, solution pH, amount of generated sludge, electrical energy consumption and aluminium concentration in the treated solution after electroprocessing versus time are shown in Table 5.

At a constant current density of 30 mA/cm^2 and an electrolysis time of 20 minutes the concentration of nickel ions rapidly fell under the admissible limits.

Compared to the removal from synthetic solutions (Tables 3 and 4) the removal rate of the studied metal from wastewater

seems to be slower. This should be attributed to the presence of the organic compounds, which also compete for absorption on the Al(OH)$_3$ flocks resulting in a substantial reduction of the metal ions removal. As known, various other organics, beyond complex former, are added to the electroplating baths, such as brighteners, buffering and wetting agents. The COD of the wastewater decreased from the initial value of 324 mg/L to 126 mg/L after 25 min, which corresponds to a removal efficiency of about 61 %. Consequently, electrocoagulation is an effective method for removing simultaneously both, heavy metals and organic compounds from wastewater.

Table 5. Residual concentration and removal efficiency of nickel ions with time during the electrocoagulation treatment of the electroplating wastewater sample. Current density = 30 mA/cm2, initial nickel concentration = 215 mg/lit, solution volume = 250 ml.

Time	Residual Ni^{2+} concentration (mg/lit)	Removal efficiency	pH	Al consumption	Sludge amount	Energy consumption	Al concentration
0	215.0		6.5				
5	161.2	25.0	6.0				
10	94.7	55.9	5.8				
15	37.3	82.6	6.4				
20	1.7	99.2	7.1	1.141	7.452	12.772	350

3.3 Electrode mass loss and energy consumption

The costs in wastewater treatment with electrocoagulation are the expenditure on mass loss of electrodes and the electrical energy consumption. The mass loss of the aluminium anode *mAl* can be calculated from equation (1) using the Faraday's law:

$$mAl = \frac{I \cdot t \cdot M}{z \cdot F \cdot mNi} \qquad (1)$$

where

I = current intensity (A)
t = time (s)

M = Molecular weight of Aluminium (g/mol)
z = number of electrons transferred in the reaction Al → Al^{3+} + 3e$^-$
F = Faraday's constant (96500 Cb/mol)
mNi = mass of nickel removed from wastewater.

The calculated mass loss of the sacrificial aluminium anode for electrocoagulation of the treated electroplating wastewater is 0.936 g Al/g Ni removed from wastewater. However, due to additional chemical dissolution of aluminium in alkaline and acidic conditions in the vicinity of cathode and anode respectively, the experimentally measured aluminium consumption is somehow higher amounting to 1.141 g Al/g Ni. Aluminium electrode consumptions after electrocoagulation treatment for all synthetically prepared nickel containing wastewater samples are given Tables 3 and 4.

Similarly, the electrical energy consumption E is calculated from equation (2):

$$E = \frac{U \cdot I \cdot t}{mNi} \qquad (2)$$

where

U = voltage (Volts)

The energy consumption for electrocoagulation treatment of the electroplating wastewater amounts to 12.772 wh/g Ni removed from treated wastewater. Electrical energy consumptions for the treated synthetically prepared wastewaters are shown in Tables 3 and 4.

3.4 Sludge ammount

The precipitated sludge was collected, dried at 103 ^{o}C for 24 h, cooled in a desiccator and weighed. It consists of nickel in form of $Ni(OH)_2$ and aluminium in form of $Al(OH)_3$ in case of the treated synthetically prepared samples and additionally of absorbed organic substances in case of the treated actual electroplating wastewater. Its amount is based on the Faraday's law. The measured sludge amounts for the electrocoagulation treatment of the synthetically prepared

solutions and the actual electroplating wastewater are given in Tables 3, 4 and 5 as mass in g of Total Suspended Solids per mass in g of nickel removed from treated solution (gTSS/gNi). The electrocoagulation treatment produces apparently less sludge compared to that produced by the conventional chemical coagulation process.

4. 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 4-8. Removal rate increased with increasing applied current density. The nickel concentrations in synthetic solutions and industrial wastewater fell under the admissible limits in only 15 and 20 minutes respectively. 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.

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