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

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Nickel bearing industrial effluents

Nickel ions are released into the environment from industrial activities:

- ✓ *electroplating*
- ✓ *metal finishing*
- ✓ *textile dyeing*
- ✓ *agriculture*

Electroplating effluents may contain nickel up to*:*

500 mg/L

Permissible limit of nickel in effluent discharge:

2 mg/L

Methods for nickel removal from wastewater

Nickel can be removed from wastewater by:

- *adsorption*
- *biosorption*
- *ultrafiltration*
- *ion exchange*
- *precipitation*
- *chemical coagulation*

and by electrochemical methods:

- *electrodialysis - electrodeionization*
- ***electrowinning***
- ***electrocoagulation***

Objective of present work

The present work proposes an integrated process to recover pure metallic nickel from nickel containing industrial galvanic effluents.

The process involves three subsequent steps:

i. ***Electrocoagulation*** *treatment of nickel galvanic effluent and production of nickel free water and a sludge containing* $Ni(OH)_2$ *and* $Al(OH)_3$*.*

ii. ***Acid digestion*** *of the sludge followed by controlled pH increase to preferentially precipitate the* $Al(OH)_3$*.*

iii. ***Electrowinning*** *for recovery of pure metallic nickel.*

i. *The initial Ni^{2+} ion concentration of 95 mg/L in effluent was treated by electrocoagulation leading to reduction of Ni^{2+} ions in the effluent under the permissible limits (<2 mg/L) and to a $Ni(OH)_2$ / $Al(OH)_3$ sludge.*

ii. *The produced $Ni(OH)_2$ / $Al(OH)_3$ sludge was then treated first with H_2SO_4 for digestion and then by NaOH for precipitation and separation of $Al(OH)_3$, while Ni^{2+} ions remain in solution.*

iii. *Electrowinning of the obtained concentrated 1000 mg/L Ni^{2+} ions containing solution, 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 otherwise would result in landfill.

Brief description of electrocoagulation

Electrocoagulation is a process consisting of creating metallic hydroxide flocks by **electrodissolution** of soluble anodes of **Al** or **Fe.**

The main reactions with **Al** sacrificial anode produce **Al^{3+}** ions, at the anode and hydroxide ions, **OH^-** as well hydrogen gas at the cathode:

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

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \qquad \text{(cathode)}$$

The generated **Al^{3+}** and **OH^-** ions react to form the coagulant, **$Al(OH)_3$**

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3$$

Additionally, a part of pollutants is removed by **electro-flotation** by the cathodically generated hydrogen gas bubbles.

Bivalent heavy metal ions, such as **Ni^{2+}** are removed by adsorption by the coagulant $Al(OH)_3$

Furthermore, they combine with the electrochemically generated **OH^-** ions and precipitate as insoluble hydroxides:

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2\downarrow$$

Organic substances expressed as **Chemical Oxygen Demand (COD),** which are also present in nickel electroplating effluents, are also adsorbed by the coagulant $Al(OH)_3$.

Consequently, **COD** is also reduced.

Both phenomena act <u>synergistically</u> leading to a rapid simultaneous removal of nickel and organic pollutants from treated wastewater.

Apparatuses:

- ***Atomic Absorption Spectroscopy Apparatus*** (Perkin Elmer 5100)
- ***COD apparatus*** (Thermoreactor, TR 420, MERCK).
- ***Conductometer*** (WTW)
- ***pH-meter*** (Hanna)
- ***Electrochemical cell***: Cylindrical glass cell of 500 mL, solution volume 200 mL
- ***Electrodes***: Three aluminum plates ***(electrocoagulation)*** and two outer nickel plates as cathodes and one middle Ti/Pt as anode ***(electrowinning)*** with an effective area of 30 cm^2 each.

Main characteristics of the actual galvanic nickel wastewater

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

Effect of initial pH on (%) removal of Ni

- **pH<2** : ***low removal percentage of Ni and COD***
- **pH 4 -10** : ***high and almost constant removal percentage***
- **pH>10** : ***slight decrease in removal efficiency***

The ***value of pH changes*** during the process due to ***hydrogen evolution*** and generation of ***OH^- ions*** at the cathodes.

In alkaline medium (pH>8) ***the final pH does not change markedly*** because the generated **OH^-** combine with the generated **Al^{3+}** and **Ni^{2+}** ions forming the insoluble coagulant flocs **$Al(OH)_3$** and nickel hydroxide **$Ni(OH)_2$**

Therefore, the electrocoagulation process was conducted in the ***optimum pH range 4-10.***

Effect of initial solution pH on (%) removal of Ni

pH	*Ni removal (%)*
2	27.8
3	83.2
4	96.6
5	98.5
6	98.7
7	98.2
8	99.2
9	99.3
10	99.1

Effect of current density

The **applied current density** determines :

- ***the coagulant dosage rate***
- ***the bubble production rate and size***
- ***the coagulant flocs growth***

resulting in a faster removal of pollutants.

Measurements carried out at current densities **5-15 mA/cm^2**, constant initial concentration of **Ni=95, COD=315 mg/L** and initial **pH= 4.5**

The **removal rate** of pollutants ***increases*** with ***increasing current density***. In only a few minutes of electroprocessing the concentration of nickel is almost quantitatively eliminated **(>99%).**

At the same time COD decreases by about **63%**

Removal percentage of nickel with time of electrocoagulation and applied current density

	(5 mA/cm^2)		(10 mA/cm^2)		(20 mA/cm^2)	
Time (min)	Residual Ni^{2+} Conc. (mg/L)	Removal efficiency (%)	Residual Ni^{2+} Conc. (mg/L)	Removal efficiency (%)	Residual Ni^{2+} Conc. (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				

Reduction of wastewater COD with electrocoagulation time

- Various organics (expressed as COD) are added to the galvanic electroplating baths , such as:

✓ ***complex formers,***

✓ ***brighteners,***

✓ ***buffering agents,***

✓ ***wetting agents***

- Organic compounds contained in the treated wastewater sample also compete for absorption on the $Al(OH)_3$ flocks.
- COD decreased from 315 to 106 mg/L after 30 min at the current density of 20 mA/cm^2, corresponding to 66.3 % removal efficiency.
- Consequently, electrocoagulation is an effective method for removing simultaneously both, ***heavy metals*** and ***COD*** from wastewater.

Reduction of wastewater COD with electrocoagulation time

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

Sludge leaching

- The precipitated sludge was collected, dried at 80 ^{o}C for 24 h, cooled in a desiccator and weighed. It consists mainly of ***$Ni(OH)_2$*** and ***$Al(OH)_3$*** and some absorbed ***organics*** originated from the organic additives contained in the electroplating wastewater.
- The amount of the produced sludge is based on the Faraday's law. Compared to the conventional chemical coagulation process, electrocoagulation produces less sludge.
- 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.
- The ***nickel*** and ***aluminum*** extraction occurred in only a few minutes of leaching time and amounted to ***98*** and ***92 %*** respectively.

Leaching reactions

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

$$2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O$$

Leaching of electrocoagulation sludge at various temperatures and pHs

Temperature (^oC)	***[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

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 product*** of the hydroxides:

$Ni(OH)_2$ ($K_{sp}=1.58x10^{-14}$) and ***$Al(OH)_3$ ($K_{sp}=1.99x10^{-33}$)***

From the same initial solution of ***10^{-2} M*** for 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***

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 ***pH=4.8***.

At pH=4.8 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 nickel electrowinning.

Recovery of metallic nickel by electrowinning

The cylindrical electrowinning reactor was equipped by a thermostatic water jacket and thermostatic bath.

Electrowinning experiments were conducted at 40 ^oC in galvanostatic operations and stirring conditions of 200 rpm.

By applying constant current densities of ***5, 10 and 20 mA/cm²***, 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 ***<5 mg/L***.

This Ni^{2+} concentration of <5 mg/L in the treated solution of small volume can further be decreased to ***<2 mg/L*** by pouring the solution into the initial wastewater prior to the electrocoagulation treatment.

It was estimated that about ***1.5 Kg of pure metallic nickel*** could be obtained from ***10 Kg of electrocoagulation sludge***.

Reduction of Ni^{2+} ion concentration by electrodeposition in metallic form versus time and current density

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		

Conclusions

Electrocoagulation with aluminium electrodes is a safe and convenient route for effective removal of nickel from wastewater.

Best removal capacity was achieved in the pH range 4-10. The nickel concentrations in the treated industrial wastewater fell under the admissible limits (2 mg/L).

COD present in electroplating wastewater was also removed.

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.

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.

Thank you for your attention