

Treatment of hydrocyanic galvanic effluent by electrocoagulation: Optimization of operating parameters using statistical techniques and a coupled polarity inverter

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Abstract—The treatment of hydrocyanic galvanic effluent with Zn, Ni and Cu ions by electrocoagulation (EC) using aluminum electrodes and a polarity inverter was evaluated. 32 experiments were performed and the optimal operating conditions were obtained using statistical analysis: 30 minutes, 5.00 g/L NaCl, 1 cm between electrodes, electrode surface area of 104 cm²/L and current density of 8 mA/cm². The results for removal with the polarity inverter were: 99.55% total cyanide, 22.49% total nickel, 52.66% total copper and 100% total zinc. After the EC experiments, localized and general corrosion of the aluminum electrodes was evaluated both internally and externally by SEM. Contaminant removal was confirmed by X-Ray powder diffraction (XRD) and Fourier transform infrared (FT-IR) which demonstrated the presence of contaminants in the galvanic sludge generated in the process.

Keywords: Aluminum Electrodes, Electrocoagulation, Electrolysis, Hydrocyanic Galvanic Effluent, Polarity Inverter

INTRODUCTION

Galvanization is a remarkable technique in an industrial setting due to the variety of coatings made possible with this metal surface treatment. Even though the main goal of this process is to improve corrosion resistance, it may be also used for aesthetic purposes.

Despite the environmental problems and the toxicity of the cyanide ion, C≡N[−] or CN[−], it is still used in electroplating due to its ability to solubilize metals by complexation, in addition to being simple to operate, low cost and generating adherent, uniform and ductile deposits [1]. Most formulations used in copper electrodeposition baths may employ cyanide electrolytes.

In this way, cyanide could be present in industrial effluents in various forms: ions (CN[−]), molecular compounds (HCN), salts and metal complexes [2,3]. The complexes are soluble and they release the complex ion M(CN)_x[−] instead of the free cyanide, according to the chemical kinetics presented in Eq. (1) [4]:



Since the effluents originating from the galvanic industries represent a pollutant overload for the environment, the industry has to comply with the current Brazilian environmental laws and regulations at the time of effluent disposal. Conventional methods for treating cyanide effluents aim to degrade and/or convert cyanide into a less toxic form, usually cyanate. These treatments should be performed along with chemical precipitation for metal removal, where alkaline chlorination and hydrogen peroxide oxidation are the most efficient methods. However, these processes are relatively

expensive due to the amount of chemical products needed, and, consequently, elevated levels of galvanic sludge are generated.

In this context, the EC process is presented as an alternative effluent treatment method, which has been described as potentially effective in the treatment of various types of effluents with high removal efficiency, which also can be used as a pre-treatment [1,5-8].

This process is based on the electrochemical method of electrolysis for treating effluents in which the oxidation of the metal electrode is responsible for the formation of the coagulating agent [9-12]. The center of the reactions is an electrochemical reactor, with metal electrodes, usually plates of aluminum or iron, in which ions are generated due to the applied electric potential. This step is part of the anodic process wherein metal is oxidized - in this case, metallic aluminum, as expressed in the oxidation Eq. (2):



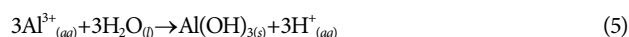
The electrolysis of water also occurs at the anode with oxygen evolution:



Meanwhile, the equation of water hydrolysis occurs at the cathode:



Thus, the coagulation step which consists in the production of hydroxide aluminum, is shown in the chemical Eq. (5):



The coagulant Al(OH)_{3(s)} is responsible for the removal of impurities from the effluent, because they are adsorbed on colloidal particles, yielding larger flocs. These flocs formed can be removed by sedimentation, filtration or flotation. Due to the water electrolysis,

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the electroflotation process (EF) is also obtained as a result of the applied potential, when microbubbles of hydrogen are formed at the cathode, as shown in chemical Eq. (4), allowing the flocs to be drawn to the surface.

Usually the electrodes in EC are connected in a monopolar or bipolar mode. Generally, direct current is used in EC systems. In this case, an impermeable oxide layer may form on the cathode material, for example aluminum, as well as oxidation leading to corrosion formation of the anode material. This prevents the effective current transfer between the anode and cathode, so the performance of EC reactor declines [13]. Some authors recommend employing a polarity inversion of the electrodes in the EC process, in which the current direction of the system is reversed at regular intervals [8,14]. Hence, the cathode becomes the anode and vice versa. Using this type of operating strategy leads to significant reductions in impact passivation of the cathode and increases the life of the aluminum electrodes. In a study by Crespilho et al. [14] the system where polarity was inverted every 2 minutes appeared to be more efficient in removing the color of an effluent from a coconut processing industry (around 2%) compared to the system without the pole reversal. Smoczynski et al. [8] evaluated phosphorus removal, which simulated synthetic wastewater effluents of the dairy industry. Optimal phosphorus removal (94%) was obtained when using aluminum electrodes with polarity inversion every 256 s, and current density of 30 mA/cm².

Usage of the EC process for treatment of effluents containing metal ions was investigated by several studies. High removal rates, higher than 90%, were achieved for the studied ions. Mouedhen et al. [15] evaluated the removal of zinc, copper and nickel from a synthetic effluent using aluminum electrodes. They observed that the addition of sodium chloride (electrolyte support) to the effluent caused the dissolution of the passive layer and decreased the potential required for the formation of coagulating agents, resulting in over 98% removal of the metallic ions cited above. Akbal and Camc [5] studied copper, chromium and nickel ion removal in wastewater generated during the plating process. Iron anodes and aluminum cathodes connected in a monopolar manner resulted in 100% removal of all three metal ions in 20 minutes of treatment at pH 3.0. Gatsios et al. [16] evaluated the optimization of the EC process for the purification of industrial waste containing toxic metals (Mn, Cu and Zn). Their results indicated that Cu and Zn were completely removed, while Mn exhibited equally high removal percentages (approximately 90%). Optimal results were obtained after 90 minutes of treatment by combining iron electrodes, at 2 cm distance, with an initial pH of 6.

Some authors have applied EC for the removal of cyanide. Mousavi et al. [2] aimed to remove free cyanide of synthetic wastewater by using iron anodes and aluminum cathodes arranged in a monopolar manner, and as result complete cyanide removal was attained. Hassani et al. [17] also studied the removal of free cyanide from a synthetic effluent using iron electrodes. It can be postulated that higher ferrous ion concentrations due to the application of high voltage (40 V), as well as high levels of free cyanide in the reactor, lead to more suitable operational conditions in terms of removal efficiency, yielding a 95% removal. In addition to these studies, Parga et al. [4] evaluated the recovery of copper from a

solution containing cyanide by applying the EC process with iron electrodes. They recovered 99% of copper cyanide, and the copper complex was reduced from 720 mg/L to 10 mg/L in 20 minutes.

Based on the studies discussed above, the removal of metal ions and cyanide is well understood. However, only few studies have been performed on the treatment of a cyanide electroplating effluent containing metal ions complexed with cyanide, which makes the treatment of such effluent more difficult due to its stability.

In this context, this study aimed to evaluate the efficiency of using a polarity inverter coupled to an EC reactor for treating a hydrocyanic galvanic effluent. Also, the galvanic sludge generated in the process was investigated, with the purpose of verifying the presence of any contaminant. The optimal operating conditions, which are those that proposed the highest removal of contaminants, were determined throughout the experimental planning and statistical analysis. Total removal of cyanide, copper, nickel and zinc of the experiment under the optimal conditions was compared with and without the use of polarity inverter, to verify its efficiency.

MATERIALS AND METHODS

1. Materials

A synthetic solution simulating a galvanic effluent was used to perform the experiments, and its composition was based on a wash water sample of an alkaline copper coating process containing cyanide, originating from a galvanic industry in Serra Gaucha (Gaúcho Highlands), in the state of Rio Grande do Sul, in southern Brazil. The concentrations of metal and cyanide ions were reproduced, since the wash water exhibits fluctuating compositions due to the incorporation of additives such as, degreasers, strippers, surfactants and brighteners, which in the majority of the cases are industrial compounds with unknown composition. The wash water sample was first characterized by distillation and colorimetry to determine total cyanide, while the atomic absorption spectrometry with air-acetylene flame was used to determine the metal ions, which resulted in the following composition: 55.24 mg/L of total cyanide, 1.59 mg/L of total nickel, 40.90 mg/L of total copper and 6.88 mg/L of total zinc. To prepare the synthetic solution, 7.92 g/L of nickel nitrate, Ni(NO₃)₂·6H₂O, 12.79 g/L zinc nitrate, Zn(NO₃)₂·4H₂O, 18.78 g/L of copper cyanide, CuCN, and 30.98 g/L of potassium cyanide, KCN, were added to deionized water. Afterwards, the composition of the synthetic solution was characterized, which exhibited the following composition: 66.18 mg/L of total cyanide, 1.71 mg/L of total nickel, 45.62 mg/L of total copper and 8.11 mg/L of total zinc.

The wash water sample pH ranged between 8.50±0.50, possibly due to variation in the manufacturing process. Therefore, the initial pH of the synthetic solution was adjusted to 8.00±0.20 with either HCl or NaOH (10%). The target pH was based on previous studies [9,11,15], which observed that the most efficient contaminant removal occurs at the initial pH range of 5 to 9, which is the optimal range for the formation of aluminum hydroxide (Al(OH)_{3(s)}). Furthermore, the presence of cyanide ions in solution and the likely formation of hydrocyanic acid (HCN) in an acidic medium could lead to a highly toxic compound [4].

The EC reactor was built in transparent acrylic, having a total vol-

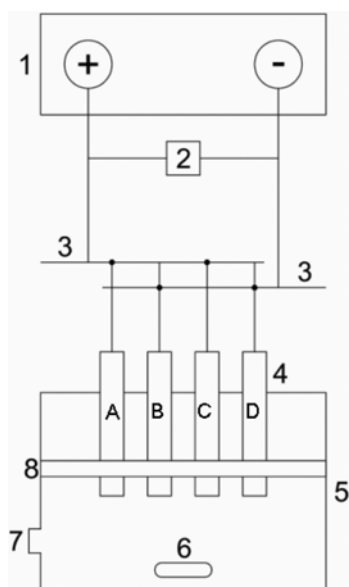


Fig. 1. Diagram of the experimental setup used for the EC process.

1. DC power
2. Inverter poles
3. Cuprum bar
4. Electrode
5. EC reactor
6. Magnetic stirrer
7. Output
8. Device for electrodes space

ume of 7 liters and a useful volume of 4 liters. Agitation was held constant at 200 rpm. All experiments were conducted in batches, at room temperature ($20 \pm 5^\circ\text{C}$) and used sodium chloride (NaCl) as supporting electrolyte. Fig. 1 shows the EC reactor and the components made for the experiments.

The configuration of aluminum electrodes was in a monopolar manner and parallel to the polarity inverter coupled to the EC reactor, which was triggered every 60 seconds, as indicated by the number 2 in Fig. 1. Rectangular plates of 99% pure commercial aluminum with dimensions of 140×100 mm and 100×100 mm and 2 mm thick were used as electrodes, which were connected to a constant current source, Minipa brand, model MPL-3303 or Tecnovolt brand, model RTMN 125082/5. Commercial copper bars of 4.75 mm in diameter was used to hold the electrodes and allow the voltage passage.

2. Methods

To understand which variables mostly influence the efficiency of the electrocoagulation process, we performed a literature review of studies applying such technique. At the same time, the variables identified as non-significant and the indicated values for some of these variables were evaluated, based on the results obtained in these

studies. Based on this review, five variables ($k=5$) were selected and the EC experiments were devised using the 2^k factorial statistical design, which considers k input variables analyzed on two levels, thus resulting in 32 experiments [18]. This procedure provides the lowest number of experiments in which k input variables can be studied on a full factorial design. The input variables and the levels that were tested are shown in Table 1. These conditions were based on previous studies [1,2,4,7,9,11,15,19-22]. The operating conditions of the experiments were generated by Statistica™ software where the randomization toll was used to prevent errors and interferences caused by external factors.

After the assays, the obtained final concentrations of total cyanide, copper, nickel and zinc were used as the system responses for the statistical analysis of the results. With a level of significance of 95% ($p < 0.05$), the effects of each input variable as well as their interaction (primary, secondary and tertiary effects were considered) and the response variables were evaluated through a variance analysis (ANOVA). The MSR surface curves and, subsequently, the desirability function were also assessed in order to obtain optimal values of the input variables under study. The experiment was executed under optimal operating conditions and after the statistical analysis it was denoted as the ECO.

In pursuance of determining total cyanide, the prior distillation and colorimetry techniques were performed according to 4500 CN C and E methods, while atomic absorption spectrometry with air-acetylene flame, according to 3030 E and 3111 B methods using a filtration step with a qualitative filter paper 80 g, was used to determine the metal ions, both methods are described in APHA [23].

At the end of the experiments, treated effluents were placed directly into specific bottles and sent for analysis. However, at the end of the ECO experiment, after 30 minutes of electrolysis the system was turned off and the effluent rested in the reactor itself for 60 minutes. In addition to this rest period, the treated effluent remained under refrigeration for 24 hours for settling and then was filtered with the filter Framex brand, number 389³, $2.00 \mu\text{m}$ porosity. After these procedures, the treated effluent was placed in special bottles and sent for analysis.

The mass loss of aluminum electrodes was quantified by gravimetric method. Surface preparation consisted in sanding with a 400 grit sandpaper. Thereafter, the electrodes were washed with deionized water, dried and weighed in a semi-analytical balance Marte brand. After the executing of experiments, the electrodes were washed again with deionized water, dried and weighed.

To evaluate the efficiency of the usage of a polarity inverter in the EC process, the removal results of the ECO experiments were compared with an experiment employing the same conditions, but

Table 1. Input variables and levels of study

Input variables	Low level (−1)	High level (+1)
Current density	1.00 mA/cm ²	8.00 mA/cm ²
Amount of supporting electrolyte (NaCl)	0.10 g/L	5.00 g/L
Electrolysis time	10.00 minutes	30.00 minutes
Distance between electrodes	3.00 cm	1.00 cm
Electrode surface area	104.00 cm ² /L	217.20 cm ² /L

without the polarity inverter system.

The SEM technique was performed on the aluminum electrodes after the ECO experiment. A Shimadzu microscope SSX-550 was used and the test specimens dimensions were of 2×2 cm. Prior to SEM analysis, the PVD (Physical vapor deposition) procedure was employed, which consists of coating the surface with a fine gold film with the objective of obtaining images with better resolution and contrast. The gold film was deposited on the Benton Desk V Metallizer.

The galvanic sludge generated in the ECO experiment was dried in a vacuum oven for 48 hours and characterized by XRD for determining the crystalline phases and FT-IR for elucidating the composition of galvanic sludge (cyanide groups, hydroxyl groups and metal oxides). The Philips X-ray diffractometer, model X'Pert MPD, equipped with graphite monochromator and rotating copper anode, operating at 40 kV and 40 mA was used. The range of angles ana-

lyzed was 5-75° 2 θ with a pitch of 0.05°/s and Cu K α radiation. Infrared spectroscopy was performed on Thermo Scientific spectrophotometer, Nicolet IS10 model with KBr at a ratio of 5% sample and 95% KBr. Spectra were recorded in the range 4,000-400 cm⁻¹.

RESULTS AND DISCUSSION

1. Optimum Operating Conditions of the EC Process

The removal results for total cyanide, nickel, zinc and copper of the experiments performed were inserted into the Statistica™ software as response variables. The final concentrations of the four response variables in each of the 32 EC experiments are shown in Table 2.

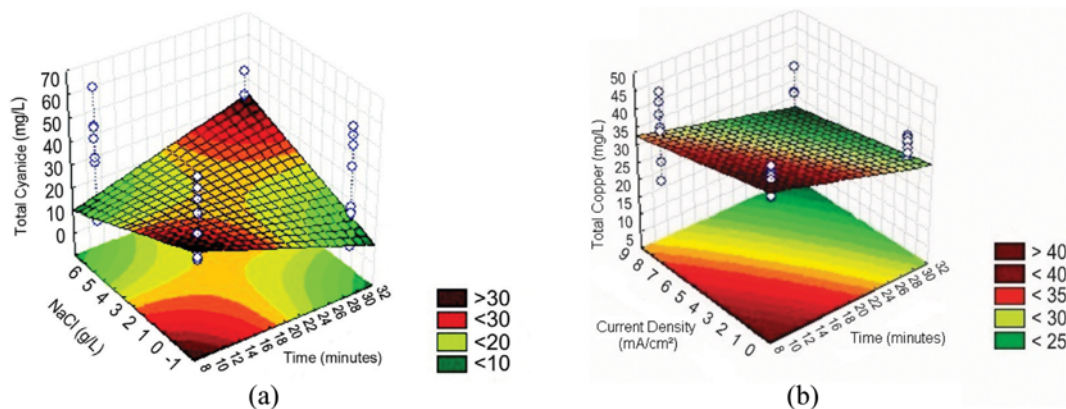
Illustrated in Table 3 are the input variables and their interactions which were significant on the total removal of cyanide and

Table 2. The operating conditions of the 32 experiments and the final concentrations of total cyanide, copper, zinc and nickel after the execution of the electrocoagulation experiments

Experiment number	Time (minutes)	NaCl (g/L)	Distance between electrodes (cm)	Electrode surface area (cm ² /L)	Current density (mA/cm ²)	Total cyanide (mg/L)	Total copper (mg/L)	Total zinc (mg/L)	Total nickel (mg/L)
1	10.00	0.10	3.00	104.00	1.00	37.77	37.72	3.06	1.74
2	30.00	0.10	3.00	104.00	1.00	54.33	34.35	0.52	1.72
3	10.00	5.00	3.00	104.00	1.00	32.05	42.75	3.12	1.59
4	30.00	5.00	3.00	104.00	1.00	3.76	36.30	0.61	1.60
5	10.00	0.10	1.00	104.00	1.00	51.73	42.20	3.49	1.71
6	30.00	0.10	1.00	104.00	1.00	21.59	35.80	0.74	1.56
7	10.00	5.00	1.00	104.00	1.00	34.06	41.02	2.35	1.63
8	30.00	5.00	1.00	104.00	1.00	39.05	34.65	0.66	1.63
9	10.00	0.10	3.00	217.20	1.00	26.68	36.50	1.07	1.60
10	30.00	0.10	3.00	217.20	1.00	58.16	30.52	0.97	1.58
11	10.00	5.00	3.00	217.20	1.00	7.59	44.78	1.73	1.61
12	30.00	5.00	3.00	217.20	1.00	5.66	33.04	0.81	1.55
13	10.00	0.10	1.00	217.20	1.00	46.43	36.82	1.45	1.60
14	30.00	0.10	1.00	217.20	1.00	49.84	31.50	2.32	1.55
15	10.00	5.00	1.00	217.20	1.00	47.89	39.10	1.15	1.67
16	30.00	5.00	1.00	217.20	1.00	27.06	29.50	0.54	1.67
17	10.00	0.10	3.00	104.00	8.00	30.11	38.72	1.13	1.62
18	30.00	0.10	3.00	104.00	8.00	40.78	17.53	0.25	1.56
19	10.00	5.00	3.00	104.00	8.00	63.97	42.52	0.24	1.45
20	30.00	5.00	3.00	104.00	8.00	1.52	29.42	0.13	1.60
21	10.00	0.10	1.00	104.00	8.00	61.27	35.26	1.50	1.62
22	30.00	0.10	1.00	104.00	8.00	23.99	14.70	0.42	1.56
23	10.00	5.00	1.00	104.00	8.00	47.33	45.15	0.51	1.51
24	30.00	5.00	1.00	104.00	8.00	10.43	29.17	0.06	1.59
25	10.00	0.10	3.00	217.20	8.00	56.51	25.62	0.48	1.70
26	30.00	0.10	3.00	217.20	8.00	6.77	11.26	0.52	1.55
27	10.00	5.00	3.00	217.20	8.00	42.60	32.42	0.08	1.64
28	30.00	5.00	3.00	217.20	8.00	28.99	37.07	1.90	1.47
29	10.00	0.10	1.00	217.20	8.00	27.72	19.95	0.21	1.59
30	30.00	0.10	1.00	217.20	8.00	20.76	5.01	0.23	1.34
31	10.00	5.00	1.00	217.20	8.00	6.58	34.05	0.13	1.55
32	30.00	5.00	1.00	217.20	8.00	28.62	20.14	0.26	1.17

Table 3. Significance results according to the variance analysis for the removal of total cyanide, nickel, zinc and copper

Parameter	Input variables	p-Value	Parameter	Input variables	p-Value
Total cyanide	Time	0.041159	Total nickel	Time	0.035633
	Time*NaCl*Distance	0.015997		Current density	0.007210
	Time*Distance between electrodes*Current density	0.047091	Total copper	Time	0.000096
Total zinc	Time	0.002197		NaCl	0.000610
	Current density	0.000039		Current density	0.000170
	Time*Electrode area	0.000368		Time*Current density	0.023659
	Time*Current density	0.004479		NaCl*Current density	0.003023

**Fig. 2. Response surface for the removal of total cyanide adjusted for the significant input variables of time and NaCl (a) and response surfaces for the removal of copper adjusted for the significant variables of time and current density (b).**

metal ions based on the ANOVA results with a 95% significance level ($p < 0.05$).

After defining the input variables and the interactions that were significant during the process of contaminant removal through ANOVA analysis, their behavior was corroborated by MSR. As an example, Fig. 2 shows two response surfaces for the removal of total copper and cyanide. The response variable analysis is of the less-is-better type and it comprises the green regions represented on the graphs.

In Fig. 2(a), which relates the input variables to the total cyanide response variable, for time and NaCl quantity variables, an adjustment has to be done on the region with 10 minutes and 5 g/L of NaCl or 30 minutes and 0.1 g/L of NaCl. In Fig. 2(b), which relates controllable variables to the total copper response variable, for time and current density variables, the adjustment had to be done in the region with 30 minutes and a current density of 8 mA/cm².

Based on the results obtained through ANOVAS (Table 3) and MSR (Fig. 2), it can be observed that the time and current density input variables are significant on the removal of the three metal ions and total cyanide. Similar results were obtained by Chawaloespho-siya et al. [24], who also used the design of experiment to analyze the correlation between the parameters on the treatment of cutting-oily wastewater by electrocoagulation flotation (ECF) process. In the same way as observed in this work under study, the authors verified that the current density and the reaction time played an important role on the process efficiency ($p < 0.005$). The other three input variables assessed (NaCl quantity, distance between the electrodes and electrode area) are only significant in some response

variables. To determine the optimal operating conditions, the desirability function was used. The overall value of this function varies from 0 to 1, and the closer to 1, the closer the response will be to the target values. As highlighted in Fig. 3, the overall function obtained was equal to 0.85453, and the desirability graphic line indicates the input variables values that lead to optimal conditions for the four system responses.

When using the desirability function, the obtained optimal operating conditions of the EC process under study were electrolysis time of 30.00 minutes, addition of 5.00 g/L supporting electrolyte (NaCl), distance between electrodes of 1 cm, electrode surface area of 104 cm²/L and applied current density of 8 mA/cm². These conditions are the same ones used to carry out the experiment number 24, displayed previously in Table 2. Therefore, this experiment was operating under the optimal conditions for the EC process. To validate these conditions, experiment 24 was repeated, conveniently named as ECO experiment, and the methodology described in Section 2.2 of this article was adopted.

Table 4 demonstrates the final concentration and the removal percentage of the four response variables obtained on the ECO experiment.

Table 4 shows that the results obtained on contaminant removal which were present in different proportions on the effluents, particularly, zinc and cyanide removal was greater than 99%.

2. Evaluation of the Efficiency of the Usage of a Polarity Inverter

The ECO experiment was also conducted without the usage of

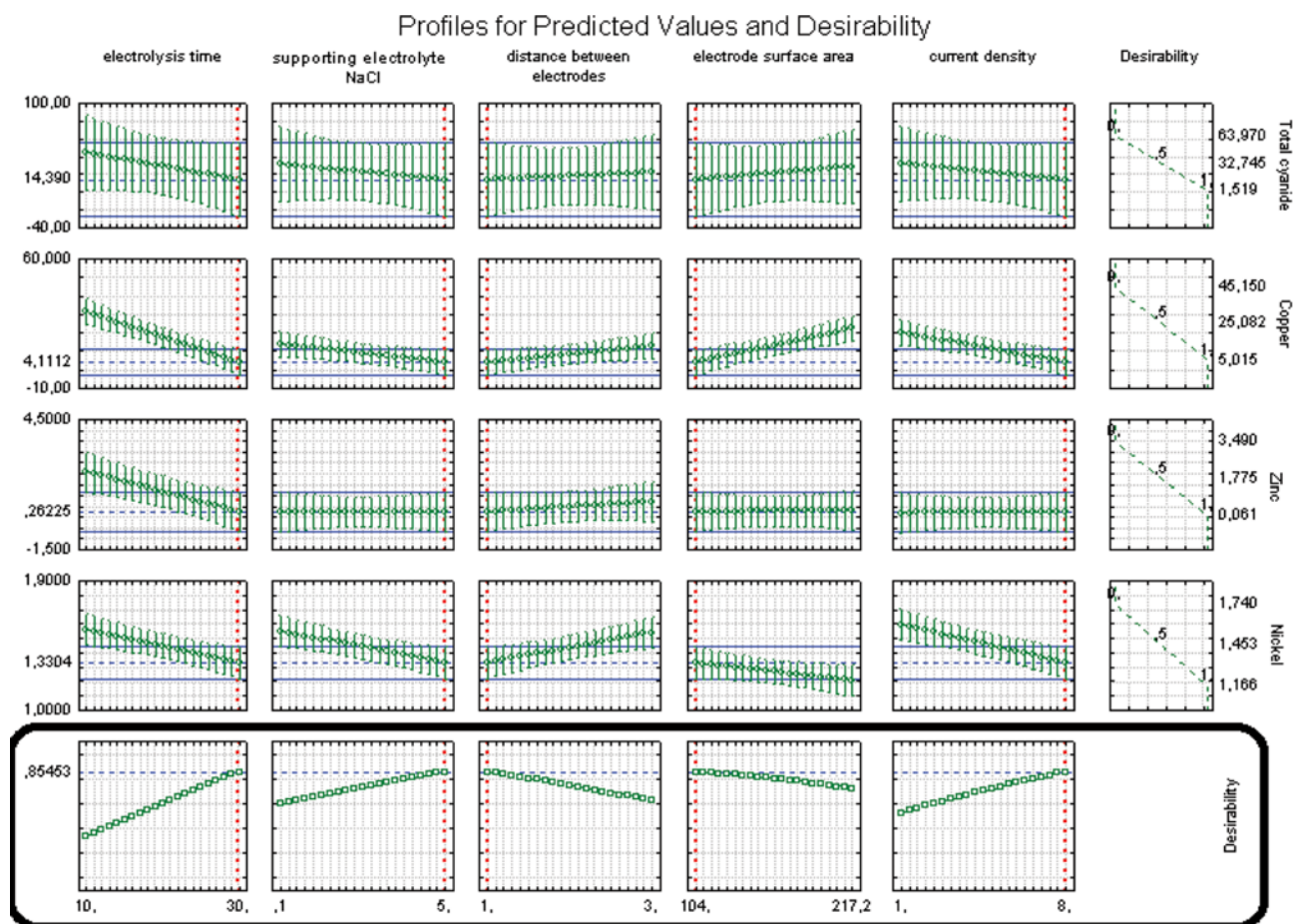


Fig. 3. Results desirability function applied to the EC process under study.

Table 4. Removal of total cyanide, nickel, copper and zinc in the ECO experiment

Parameter	ECO experiment	
	Final concentration (mg/L)	Removal (%)
Total cyanide	0.30	99.55
Total nickel	1.33	22.49
Total copper	21.60	52.66
Total zinc	n.d. (<0.034)	100.00

n.d.: not detected

a polarity inverter, in order to evaluate its efficiency in the electrocoagulation process. Fig. 4 illustrates a comparison of the removal results obtained on the ECO experiment with and without the polarity inverter.

Except for the removal of total zinc, which was close to 100% in both experiments, the usage of a polarity inverter exhibited a removal efficiency higher than 20% for total cyanide, nickel and copper when compared to the experiment in which the polarity inverter was not used. According to Miltzarek [25], the cyanide complexes formed with zinc are considered weak, which can be explained by the results on complete removal of zinc in the experiments with and without polarity inverter. In contrast, the cyanide complexes formed with nickel and copper are considered moderately strong complexes,

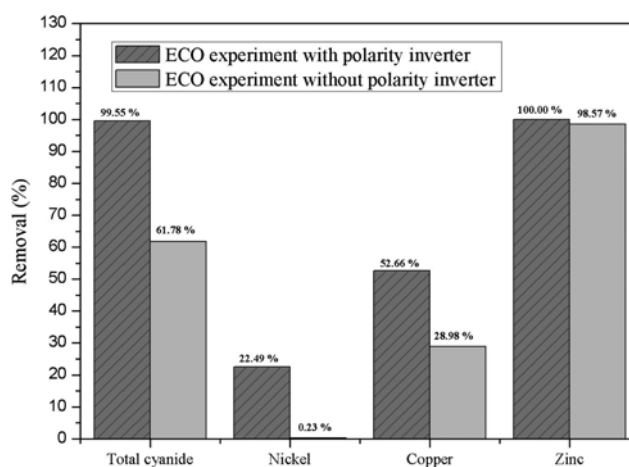


Fig. 4. Removal (%) for ECO experiment with and without the use of polarity inverter.

supporting the lower removal efficiency of the EC process for these two metal ions.

The increase in removal using the polarity inverter can be attributed to the passive film reduction of the aluminum oxide, Al_2O_3 , which forms on the surface of aluminum electrodes.

In both experiments, in order to target a current density of 8 mA/

cm^2 , 3.33 A was applied. The required voltage to generate this current was 2.5 V, by recognizing that the application of a potential of $-1.598 \text{ V}_{(\text{ECS})}$ leads to a reduction of the passive film, according to the Eq. (6) [14]:



It can be suggested that under these potential conditions applied, reaction (6) was favored and the decrease of resistivity in the system enhanced the ability of the reactor to generate the coagulating agent and it increased the contaminant removal efficiency.

Ozyonar and Karagozoglu [26], who applied the direct pulse current (DPC) mode in the treatment of electrocoagulation pretreated coke wastewater and electrochemical peroxidation processes, found similar results, which were proposed to control passivity. Their results showed that the EC process using the DCP mode was more efficient

than a DC mode with slower polarization and passivity, thereby getting better pollutant removal efficiencies.

Passivity is caused by the buildup of metal oxides on the surface of the electrodes leading to an increase in the resistance to the electrolytic process. A study on electrocoagulation by alternating pulse current (APC) was carried out by Keshmirizadeh et al. [27] with the objective of Cr(VI) removal. The authors concluded that the APC mode was more efficient than the direct current (DC) mode with a lower anode over-voltage, a slower anode polarization and passivity, and a lower tank voltage. The operating time was about 25% less when the APC mode was used. Because of the reduction in operating time, less power (or energy) was consumed making the APC mode more cost effective. Similarly, Bernal-Martínez et al. [28] evaluated the effect of continuous and pulse in situ iron addition onto the performance of an integrated electrochemical-ozone

Table 5. Mass loss (g/m^2) for the four electrodes used in the ECO experiments, with and without the use of polarity inverter

Experiment	Mass losses (g/m^2)				
	Electrode A	Electrode B	Electrode C	Electrode D	Average
ECO experiment <u>with</u> the use of polarity inverter	26.44	42.79	48.08	27.88	36.29
ECO experiment <u>without</u> the use of polarity inverter	26.92	41.83	43.27	24.52	34.13

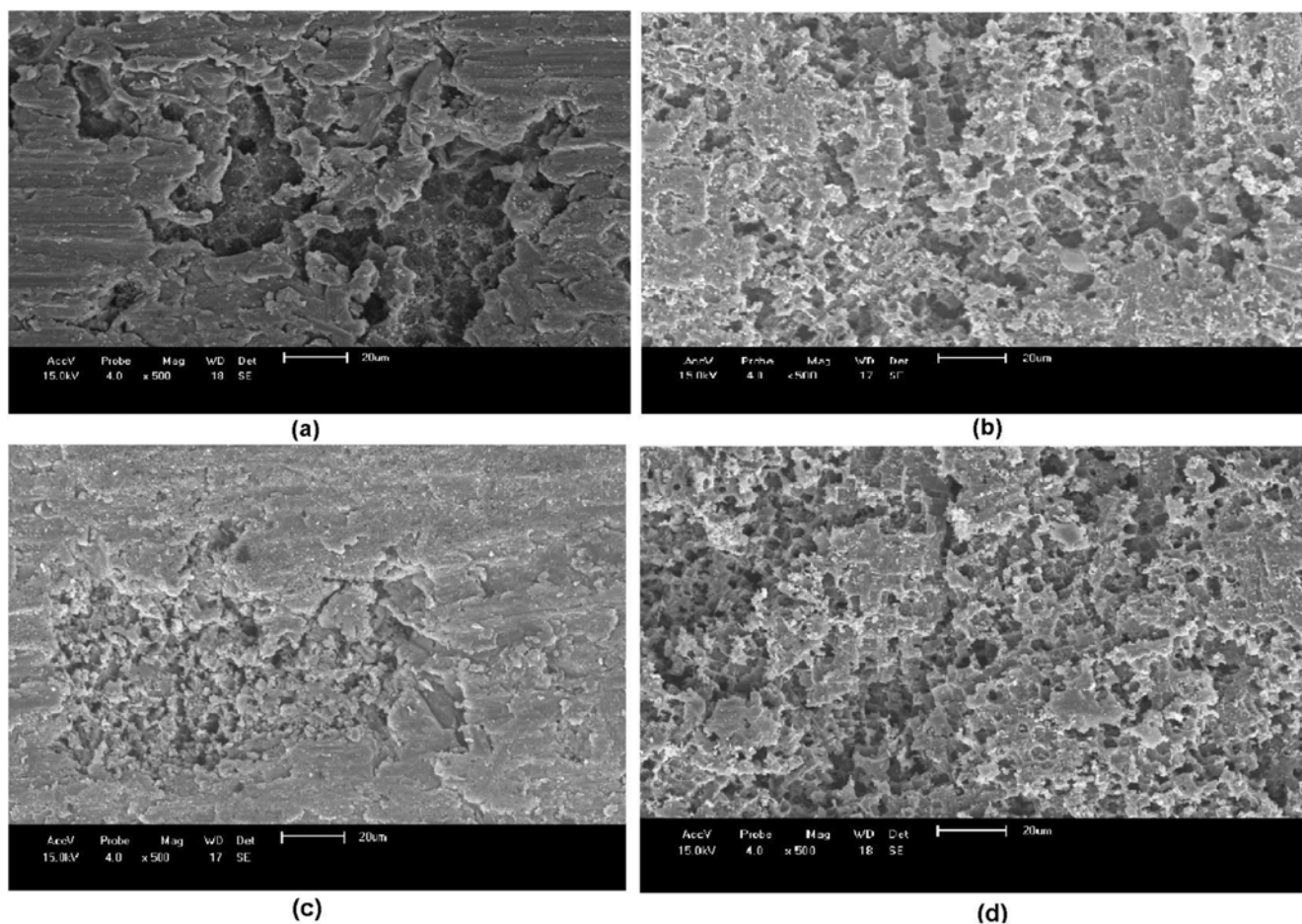


Fig. 5. SEM of the surface of the aluminum electrodes A and D used in ECO experiment, (a) external surface electrode A, (b) internal surface electrode A, (c) external surface electrode D and (d) internal surface electrode D.

reactor for wastewater treatment. The authors concluded that the pulsing operation mode was twice faster and consumed approximately half the energy than the energy required for the continuous electrocoagulation to reach similar COD, color and turbidity values. They ascribe these results to either the decreased passivation or to the different reaction kinetics expected to occur during the electrocoagulation process.

Yang et al. [29] also studied the behavior of dissolution/passivation and the transformation of passive films during the Fe-EC process for Cr(VI) treatment. The study found that an alternating pulsed current of 590 seconds results in a more unstable film when compared to a direct current sample, therefore proving that this strategy generated a non-protective and defect-formed film which led to the dissolution of iron.

Table 5 depicts the mass loss for each of the four electrodes in both ECO experiments with and without the polarity inverter. The electrode arrangement in the reactor is demonstrated in Fig. 1. The experiment with the polarity inverter showed higher electrode mass loss relative to the experiment without this component.

In the experiment without the polarity inverter, a mass loss was observed even at the cathodes, indicated by electrodes B and D. This mass loss can be attributed to a chemical attack caused by hydroxyl ions formed during the hydrolysis of water [8,11,15].

The greatest mass loss of aluminum electrodes and, consequently, the greatest amount of coagulants in solution can be seen as one of the factors influencing the higher efficiency of contaminant removal obtained in the ECO experiment with the polarity inverter. This outcome is directly associated with the reduction of the Al_2O_3 film. Similar results were found in the Gatsios et al. [16] study regarding the optimization of the EC process applied for the purification of industrial waste from toxic metals. Residual aluminum concentrations of 8.5 mg/L and 7.9 mg/L were obtained in the treated effluent with and without the polarity inverter, respectively.

Another important observation concerning the experiment with the polarity inverter is that with each polarity reversal, the evolution of gases occurred according to Eqs. (3) and (4), which determine both the mixing regime in the vicinity of the electrodes and the electrostatic attraction of ions and/or compounds formed and present when the effluent is being treated. Such change of direction during every time interval could have caused greater interaction and, consequently, greater contact between the contaminants in the effluent and the coagulant agents being formed, hence causing increased removal efficiency when using the polarity inverter in the ECO experiment. Although Lu et al. [30] did not use the polarity inverter in their experiments, they do report the importance of the bubble formation which determines the mixture inside the reactor EC, and thus accomplishing higher heavy metal ion removal. Holt et al. [31] corroborated these results when stating that flotation was favored by increasing the bubble density, by applying electrocoagulation for the treatment of potter's clay.

Finally, Table 5 shows that the mass loss is more pronounced in the central electrodes B and C, in relation to electrodes A and D, which were positioned at the ends of the EC reactor for both experiments. The electrodes B and C have higher interaction between their two sides and the effluent being treated, therefore causing a higher mass loss of the electrodes.

3. SEM Evaluation of the Aluminum Electrodes

Fig. 5 displays the SEM analysis of the surface of aluminum electrodes A and D used in ECO experiment.

Fig. 5(a) and 5(c) exhibit the external surface of electrodes A and D, where visualized localized corrosion (pitting) can be appreciated, while Fig. 5(b) and 5(d) display the internal surface of these electrodes, revealing general corrosion. Similar results were also reported by Smoczynski et al. [8]. This behavior agrees with the results of mass loss obtained for the ECO experiment, presented in Table 5. The electrodes A and D showed less mass loss in relation to the electrodes B and C.

4. Galvanic Sludge Characterization

Fig. 6(a) depicts the diffractogram of the XRD analysis of the galvanic sludge generated in the ECO experiment and the crystalline phases that were identified. Diffraction peaks characteristic of aluminum oxides and hydroxides, most likely aluminum hydroxide structure ($\text{Al}(\text{OH})_3$), were observed, which were also detected by Drouiche et al. [10]. Thus, it was possible to demonstrate the formation of coagulant agents in the form of aluminum hydroxide in the EC process.

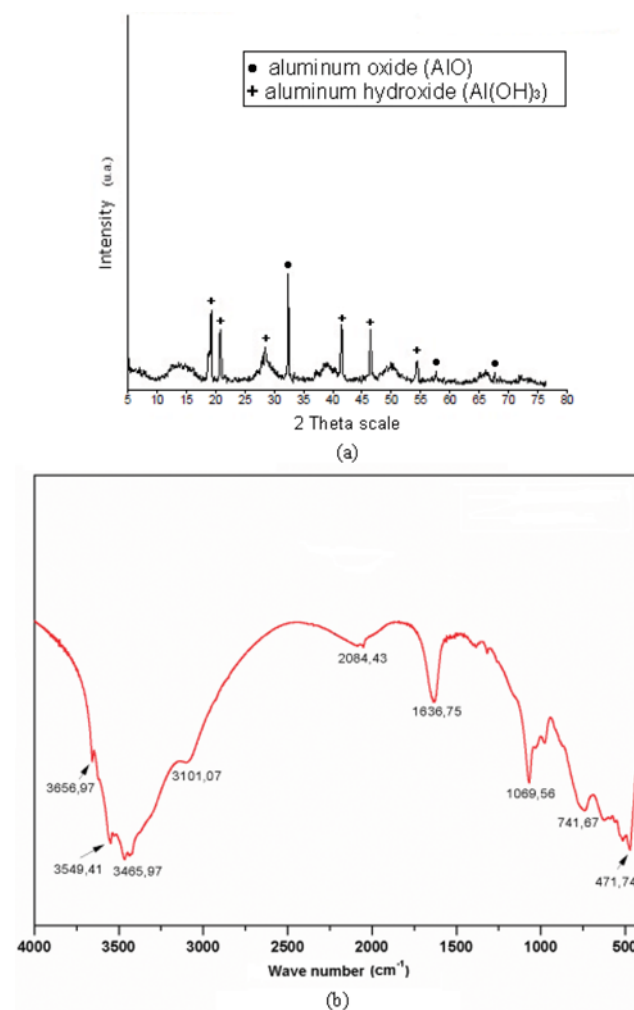


Fig. 6. (a) XRD diagram and (b) FT-IR spectrum for galvanic sludge generated in the ECO experiment.

According to the FT-IR spectrum obtained for the galvanic sludge generated in the ECO experiment, which is presented in Fig. 6(b), the bands at 3,549, 3,465 and 3,101 cm^{-1} were assigned to the stretching vibration of the hydroxyl group (OH^-). This confirms and agrees with the XRD results, indicating the predominant form of hydroxide compounds [2,9,32].

The band located at around 1,636 cm^{-1} was assigned [33] by the presence of heavy metals, relating to this study of the presence of copper, nickel and zinc. The characteristic absorption bands of the MO bond, where M is a metal ion, were identified from 410 to 610 cm^{-1} by Ardelean et al. [35] which is comprised of a band located at 471 cm^{-1} . This band confirms the results of XRD, where the presence of aluminum oxide, AlO , was detected in the galvanic sludge generated.

The band located at 2,084 cm^{-1} is attributed to triple ($\text{C}\equiv\text{N}$) and double ($\text{-C}=\text{N}$) bond, configuring the axial deformation of compounds such as cyanides, cyanates, isocyanates, thiocyanates, and isothiocyanates [34], assigned to Fe-CN precipitates in electrocoagulation studies performed by Moussavi et al. [2].

Therefore, according to these observations, the metal and the cyanide previously present in the effluent were removed from the sludge, based on the bands observed at 2,084 and 1,636 cm^{-1} .

CONCLUSIONS

The following can be concluded from the results of our study:

Through statistical analyses, after the execution of 32 EC experiments, using the desirability function, the following optimal operating conditions were obtained: electrolysis time of 30.00 minutes, amount of NaCl 5.00 g/L, distance between electrodes of 1.00 cm, electrode surface area of 104.00 cm^2/L and applied current density of 8.00 mA/cm^2 . With these operating parameters the following removal results were obtained: 99.55% total cyanide, 22.49% nickel ions, 52.66% copper ions and 100% zinc ions.

The use of a polarity inverter in the ECO experiment yielded a 20% increase in the removal efficiency of total cyanide, nickel and copper, with regards to the efficiency of this same experiment without a polarity inverter. The removal of total zinc was almost complete in both experiments; thus, no significant increase was noticed for the removal efficiency of this metal.

SEM analysis showed pitting corrosion in the external surfaces of the aluminum electrodes and general corrosion in internal surfaces. Concerning the galvanic sludge, in the analyses of XRD and FT-IR, coagulating agents in the form of hydroxides of aluminum were identified in the form of aluminum hydroxides, and the FT-IR analyses confirmed the presence of the metals copper, nickel and zinc, cyanide and cyanate.

The EC process under study is efficient for removing contaminants from hydrocyanic galvanic effluent, and the use of a polarity inverter coupled to the EC reactor increases the removal process efficiency.

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