



São Paulo - Brazil - May - 22<sup>nd</sup> to 24<sup>th</sup> - 2013

# Aca4<sup>th</sup>emmic

## INTERNATIONAL WORKSHOP ADVANCES IN CLEANER PRODUCTION

“INTEGRATING CLEANER PRODUCTION INTO SUSTAINABILITY STRATEGIES”

### **Electrodialysis as an Alternative for Treatment of Nickel Electroplating Effluent: Water and Salts Recovery**

BENVENUTI, T. <sup>a\*</sup>, RODRIGUES, M. A. S.<sup>b</sup>, KRAPP, R.S.<sup>a</sup>, BERNARDES, A. M.<sup>a</sup>, ZOPPAS-FERREIRA, J. <sup>a</sup>

*a. Universidade Federal do Rio Grande do Sul, Porto Alegre*

*b. Universidade FEEVALE, Novo Hamburgo*

*\*Corresponding author, tati.eng.biobio@gmail.com*

#### **Abstract**

Galvanic processes are one of the main activities contributors of metal discharges into the environment. The wastewater generated contains high load of salts and metals that must be treated for recovery chemicals and water, saving resources. In this work the treatment of effluents from bright nickel electroplating process by electro dialysis (ED) was studied in order to concentrate and extract nickel (Ni) and its salts and recover water for reuse, saving industrial and environmental resources. This study was started as a case requested by an European company, manufacturer of ED plants, due the operation of equipment used in the treatment of nickel plating wastewater at an Brazilian enterprise. After many tests using real and synthetic nickel plating effluent and determination of limiting current value in previous works, one bench scale electro dialysis system was evaluated, containing five compartments cells separated by four 16cm<sup>2</sup> membranes. It was used a synthetic effluent based on industrial baths composition, including salts and organic additives. Nickel extraction, pH and conductivity were evaluated for all compartments. After ED, the treated effluent was evaluated by chemical analysis for verify its quality. It was found that ED treatment generates, as product, a very low conductivity solution, allowing the reuse as rinsewater, and a concentrated solution able to fortify the bath and recover volumes lost by evaporation and drag during the nickel electroplating process.

**Keywords:** *Nickel electroplating, effluent treatment, electro dialysis, reuse.*

#### **1. Introduction**

Electroplating or metal finishing processes are associated to a large liquid effluent volume, with relatively low, although harmful, metal concentrations as Ni, Cr, Cu, Zn, etc. The water consumption in these processes is very large, and the chemicals used are expensive and come from non-renewable sources.

Among several electroplated metals, nickel is widely used for coating different materials, and it has the property of improving the corrosion resistance as well as providing decorative characteristics (Schario, 2007). The Watts' bath, composed by nickel chloride, nickel sulphate and boric acid, is the most widely

“INTEGRATING CLEANER PRODUCTION INTO SUSTAINABILITY STRATEGIES”

São Paulo - Brazil - May 22<sup>nd</sup> to 24<sup>th</sup> - 2013

used process. This electroplating process generates wastewater with nickel and organic additives that must be treated. Nickel plating effluents may contain up to  $1,000\text{mgL}^{-1}$  nickel which, according to environmental regulations worldwide, must be controlled to an acceptable level to be discharged to the environment. Several treatment processes have been suggested to the removal of nickel from aqueous wastes and the most used one is the chemical precipitation (Orhan et al, 2002).

The traditional treatment methods are not efficient, because they generate galvanic sludge that is considered a hazardous waste (Dermentzis, 2010). Nowadays the conventional effluents treatment is not established in order to obtain water in a quality, that it could be reused in the same process. From the environmental and resource saving point of views, recycling and reusing the metal wastewater in closed-loop systems should be developed. For this reason this study was carried out in order to evaluate the electrochemical treatment of nickel electroplating effluents.

The electrodialysis (ED) process is becoming a good alternative, when it is compared to the traditional wastewater treatment methods. ED is based on the selective migration of aqueous ions through ion-exchange membranes as a result of an electrical driving force (Rodrigues et al, 2008). The transport direction and rate of each ion depends on its charge and mobility, solution conductivity, relative concentrations, applied voltage, etc. Ion separation is closely related to some characteristics of the ion-exchange membrane, especially their permselectivity (Birkett, 1978). A typical ED cell arrangement consists in a series of anion and cation-exchange membranes arranged in an alternating pattern between an anode and a cathode to form individual cells. The overall result is an increase in the ion concentration in alternate compartments, while the other compartments simultaneously become depleted. The depleted solution is generally referred to as the dilute and the concentrated solution as the brine or the concentrate. The process presents the advantage of allowing the recovery and reutilization of water and chemicals used in the process. ED was developed first for the desalination of saline solutions, but other applications, such as the treatment of industrial effluents, are gaining increasing importance (Buzzi et al, 2013).

This work addresses the electrodialysis treatment of a bright nickel electroplating effluent to concentrate and extract nickel and its salts. It was evaluated the pH and conductivity for all compartments and the percentage extraction of nickel. After ED, the treated effluent was evaluated by chemical analysis for verify its quality for reuse.

## 2. Materials and Methods

### 2.1. Solutions

The electrodialysis tests were carried out with a synthetic solution simulating the rinsewater of bright nickel electroplating and corresponding to 1% of bright nickel bath in distilled water. The solution composition is shown in Table 1. Analytical grade reagents are used. This solution contains close to  $1,3\text{mg.L}^{-1}$  Ni,  $3\text{mS.cm}^{-1}$  and pH 4.4, and it fed the central compartment of electrodialysis cell, where it was treated. To maintain the conductivity in the system, solutions of sodium sulphate ( $\text{Na}_2\text{SO}_4$ )  $4\text{g.L}^{-1}$  ( $5.5\text{mS.cm}^{-1}$  and pH 5) fed the other cell compartments. Drops of HCl analytic grade was added to the effluent for pH correction during the electrodialysis treatment.

**Tab.1.** Composition of the nickel synthetic wastewater.

Compounds	Concentration
$\text{NiCl}_2$	$0.65\text{ g.L}^{-1}$
$\text{NiSO}_4$	$2.75\text{ g.L}^{-1}$
$\text{H}_3\text{BO}_3$	$0.45\text{ g.L}^{-1}$
AditivoA® (brightener)	$0.02\text{ mL.L}^{-1}$
Nimac14® (carrier at low current density)	$0.4\text{ mL.L}^{-1}$
Nimac33® (carrier at high current density)	$0.4\text{ mL.L}^{-1}$
Clarion II® (surfactant)	$0.01\text{ mL.L}^{-1}$

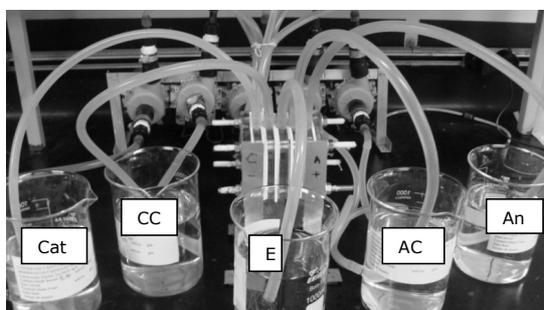
## 2.2. Analytical Methods

In all the experiments, a conductometer (8361 AZ Instrument) was used to measure the electrical conductivity and temperature of samples. A pHmeter pH-TEC PHS-3B was applied for measuring pH solutions.

Nickel concentrations were determined by Flame Atomic Absorption Spectrophotometer using an analytical Varian FS-240 Spectrometer. The cations and anions analysis was performed using the Ionic Chromatograph DIONEX ICS-3000. The presence of organic compounds was verified by UV-Vis analysis using a Molecular Absorption Spectrometer T80+UV-VIS PG Instruments Ltd.

## 2.3. Apparatus and experimental procedure

The treatment was conducted in a five-compartment ED cell (Fig. 1). According to previous studies (Benvenuti et al., 2012), it was applied  $1.8\text{mA}\cdot\text{cm}^{-2}$  current density to treat all Ni solutions. This value was chosen because is above the limiting current density (Buzzi et al, 2013; Benvenuti et al, 2012).



**Fig.1.** Electrodeposition system used for the treatment of Ni solutions. (Cathode solution (Cat), Cations Concentrate solution (CC), effluent (E), anode concentrate solution (AC) and Anode solution (An)).

Each container with 1L of solution was connected to a pump for the recirculation of the solutions ( $80\text{L}\cdot\text{h}^{-1}$ ). In both ends of the cell, the electrodes, cathode and anode, were both  $16\text{cm}^2$  Ti plate coated with  $\text{Ti}_{0.7}/\text{Ru}_{0.3}\text{O}_2$ . The tests were performed under room temperature (about  $25^\circ\text{C}$ ). Cationic – Ionac MC-3470 and anionic – Ionac MA-3475 membranes, with a surface area of  $16\text{cm}^2$ , were used. The stack was made in clear acrylic and the membranes separate the five compartments: there was one cation-exchange membrane (C) and 3 anion exchange membranes (A); the stack configuration was (Cat-)A-C-A-A(-An).

Three ED treatments were carried out during the necessary time for check the Ni extraction and until the effluent became a diluted solution, reaching the conductivity as low as the water supply. The same membranes were used for three tests.

## 2.4. Data analysis

The purpose of the experiments was to study the effects of several parameters on ED cell performance for Nickel, and other cations and anions removal. Table 1 refers to concentration changes in the effluent. Data for concentrate and electrode rinse solution will not be presented in this article.

The demineralization rate (DR) reflects the total amount of salts removed. It can be calculated from conductivity values using the following equation (Casademont, 2008; Wang, 2009):

$$\text{DR}\% = [1 - (\text{EC}_t / \text{EC}_0)] \cdot 100 \quad (\text{Eq.1})$$

Where  $EC_0$  and  $EC_t$  are, respectively, the conductivity of the dilute before and after treatment (expressed in  $mScm^{-1}$ ).

Percentual extraction (PE%) for Ni, and cations and anions detected by ionic chromatography, was evaluated using the equation below:

$$PE\% = [(1 - (M_i^f / M_i^0)) \cdot 100] \quad (\text{Eq. 2})$$

Where  $M_i^0$  is the ion concentration in the effluent in the beginning of the experiment and  $M_i^f$  is the ion concentration in the effluent at the end of the experiment.

### 3. Results and Discussion

Tab. 1 shows the results obtained for nickel effluent treatment by the three ED treatments. The percent extraction (PE%) was determined for nickel and for the species detected by ionic chromatography, such as chloride, sulphate, sodium and potassium. The demineralization rate is presented in the Tab.1 too.

**Tab. 1.** Electrodialysis treatment of nickel electroplating effluent: concentration, percentual removal (PE%) and demineralization rate (DR%).

Treatment/Parameter	ED 1	ED2	ED3	Mean	SD
<b>Treatment Time (h)</b>	44.55	37.60	37.55	39.9	±4.03
<b>Final Conductivity (mS.cm<sup>-1</sup>)</b>	0.10	0.23	0.18	0.17	±0.06
<b>DR%</b>	96.75	92.77	94.33	94.61	±2.01
<b>PE% [Ni<sup>2+</sup>]</b>	99.93	96.46	95.90	97.43	±2.18
<b>PE% [Ni<sup>2+</sup>].h<sup>-1</sup></b>	2.24	2.57	2.55	2.44	±0.18
<b>PE% [Cl<sup>-</sup>]</b>	96.61	95.04	99.81	97.16	±2.43
<b>PE% [SO<sub>4</sub><sup>2-</sup>]</b>	99.10	97.77	99.27	98.71	±0.82
<b>PE% [Na<sup>+</sup>]</b>	92.59	96.95	99.14	96.23	±3.34
<b>PE% [K<sup>+</sup>]</b>	89.41	97.89	96.98	94.76	±4.66

The rinsing water is, in electrodeposition process, the assurance of product quality. It acts in the dilution or depletion of salts dragged out for pieces through one bath to another. These salts influence negatively the coating obtained by electrodeposition. The acceptable concentration of the electrolyte dragged to the next step is around  $1mg.L^{-1}$  to  $100mg.L^{-1}$ , depending on the bath type and composition. The last rinsewater is very important, because it can influence on the surface coating quality, changing its mechanical or corrosive characteristics (CPRH, 2001).

For this reason it is so important to apply and enhance clean technologies that enable appropriate treatment for electroplating rinsewater and allow the reuse of these waters in the production process, such as rinsewater again, allowing operation in closed circuit, reducing financial and environmental costs and recovering components of galvanic baths.

The mean time necessary for carry out an effective electrodialysis for treat 1L of synthetic nickel electroplating effluent, at lab scale, using  $16cm^2$  of ion-exchange membranes area, was 39.9 hours, resulting in a high demineralization rate, about 95%. Comparing the three tests, the drop in conductivity was satisfactory reaching values similar to served water. According to values obtained for

DR%, which kept a small deviation for the three tests, the ED treatment showed a reasonable extraction for all ions in the solution, making good quality water for reuse.

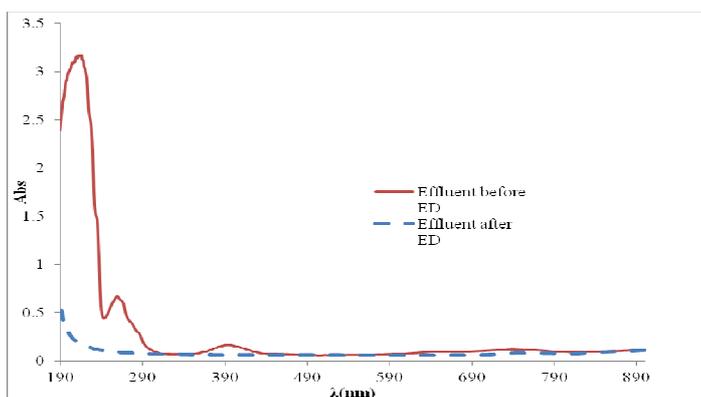
All ions had a good percent extraction. Some of them, as sodium and potassium, had low concentrations (less than 140 and 60 mg.L<sup>-1</sup> respectively) coming from the distilled water applied for produce the synthetic effluent, natural contaminants of NiCl<sub>2</sub>, NiSO<sub>4</sub> and H<sub>3</sub>BO<sub>3</sub>, addition to the organic additives, commercial formulas, which composition is not known. After the ED treatment the concentration of these ions was less than 10mg.L<sup>-1</sup>.

The values obtained for removal chlorides and sulphate ions confirm the possibility of reuse. These ions compose naturally bright nickel baths in high concentrations. However, if in excess in the rinsewater, can damage the coating, and accelerate the corrosion process. Excess of sulphate ion can make acidic water and chlorides are known for their high corrosive activity on metals.

The PE% for nickel was satisfactory. The final concentrations remained below 48mg.L<sup>-1</sup>. This concentration is above the allowed limit for disposal of treated effluents in Brazil, according to CONAMA 357/2005 (Brasil, 2005), however, both the clear visual, as the conductivity indicate the good quality of the treated effluent for reuse as rinsewater.

According to the necessary time for Ni extraction, it was verified that ED treatments performing at longer times represents greater energy expenditure, since the demineralization rate obtained after the treatment is similar to the tests shorter. However, the longer treatment time reached the standards for effluent discharge, and Ni concentration was less than 1mg.L<sup>-1</sup>. This observation indicates the higher cost required for treatment to dispose of the effluent, rather than the reuse.

Regarding the additives components, their inorganic portion was satisfactorily removed according to the ionic concentration observed in the effluent before and after the ED treatment. The organic portion, like the most organic molecules, existing in natural waters and effluents, is negatively charged, may be transported to the anions concentrate compartment through the anionic membrane, or has been adhered to the anionic membrane, causing fouling (Lindstrand et al, 2000). As the concentration of additives in the effluent is low, performing a reverse electrodialysis (EDR), at predetermined time intervals, can minimize the occurrence of fouling. The qualitative assessment of raw Ni plating effluent and the effluent treated for ED performed by UV-Visible spectrometry indicates the removal of organic compounds after ED, through the reduction of the absorbance bands for the organic additives, as is seen in Fig.2.



**Fig.2.** UV-Vis spectra for synthetic Ni plating effluent before and after the ED treatment applying 1.8mA.cm<sup>-2</sup> for 39.9h indicated the reduction in organic compounds absorbance after ED treatment.

Applying a clean technology as electro dialysis for treat nickel electroplating effluent it can be produced high quality treated water for reuse. This process does not depend of chemicals addition, such as the conventional treatment consequently, does not generate galvanic sludge, a toxic waste from the electroplating industry and, furthermore, the water quality obtained is suitable for reuse as rinsewater in the electroplating process.

#### 4. Conclusions

Electrodialysis is a clean technique able to produce dilute and concentrated solutions from a contaminated started solution. The dilute solutions generated after three tests for treat synthetic bright nickel electroplating effluent were evaluated. This process has already been applied for treat electroplating effluents around the world. This work only reinforces the opportunity to reduce costs and consumption of chemicals and natural resources provided by the application of technology to ED

These solutions were evaluated for the rate of demineralization and the perceptual extraction of ions in solution. It was confirmed that, the treated effluent had sufficient quality for reuse as rinsewater in galvanic process. All ions detected presented adequate concentrations for reuse, but, for discharge, the Ni concentration is still high. Even the organic compounds from the additives could be removed by ED.

Optimizing parameters for ED process has been studied for obtain a higher removal for Ni, and the energy consumption will be evaluated for an ED treatment effective and at the lowest possible cost, producing quality water for reuse in various industrial processes.

#### 5. References

Benvenuti, T., Haubert, G., Fensterseifer Jr., G., Rodrigues, M. A. S., Bernardes, A. M., Zoppas-Ferreira, J. 2012. Electro dialysis for the nickel electroplating industry from Sinos River Basin. In: 3rd International Conference on Industrial and Hazardous Waste Management. Chania. Crete: Technical University of Crete, Greece.

Birkett, J.D. Electro dialysis. 1978. In: Berkowitz JB, editor. Unit operations for treatment of hazardous industrial wastes. New Jersey: Noyes Data Co. p. 406.

BRASIL, 2005. Conselho Nacional do Meio Ambiente. Resolução nº 357 de 03/2005. <<http://www.mma.gov.br/port/conama/res/res05/res35705.pdf>>. Accessed in Feb., 2013.

Buzzi, D., Viegas, L.S., Rodrigues, M.A.S., Bernardes, A.M., Tenório, J.A.S. 2013. Water recovery from acid mine drainage by electro dialysis. *Minerals Engineering*, 40, 82-89.

Casademont, C., Farias, M.A., Pourcelly, G., Bazinet, L. 2008. Impact of electro dialytic parameters on cation migration kinetics and fouling nature of ion-exchange membranes during treatment of solutions with different magnesium/calcium ratios. *Journal of Membrane Science*. 325, 570-579.

Companhia Pernambucana do Meio Ambiente. CPRH. 2001. Agência Estadual de Meio Ambiente e Recursos Hídricos. "Roteiro Complementar de Licenciamento e Fiscalização - Tipologia Galvanoplastia". 107p. Recife, PE. Disponível em: [http://www.ana.gov.br/Destaque/d179docs/PublicacoesEspecificas/Galvanoplastia/Controle\\_ambiental\\_galvanoplastia.pdf](http://www.ana.gov.br/Destaque/d179docs/PublicacoesEspecificas/Galvanoplastia/Controle_ambiental_galvanoplastia.pdf).

Dermentzis, K. 2010. Removal of nickel from electroplating rinse waters using electrostatic shielding electro dialysis/electrodeionization. *Journal of Hazardous Materials*. 173, 647-652.

Lindstrand, V., Sudstrom, G., Jonsson, A.S. 2000. Fouling of electro dialysis membranes by organic substances. *Desalination*, 128, 91-102.

Formatado: Inglês (Estados Unidos)

Orhan, G., Arslan, C., Bombach, H., Stelter, M. 2002. Nickel recovery from the rinse waters of plating baths. *Hydrometallurgy*. 65, 1 –8.

Rodrigues, M. A. S., Amado, F.D.R., Xavier, J. L. N., Streit, K. F., Bernardes, A. M., Zoppas- Ferreira, J. 2008. Application of photoelectrochemical-electrodialysis treatment for the recovery and reuse of water from tannery effluents. *Journal of Cleaner Production*. 16, 605-611.

Schario, M. 2007. Troubleshooting decorative nickel plating solutions (Part I of III installments): Any experimentation involving nickel concentration must take into account several variables, namely the temperature, agitation, and the nickel-chloride mix. *Metal Finishing*, 105 (4), 34-36.

Wang, Q., Ying, T., Jiang, T., Yang, D., Jahangir, M.M. 2009. Demineralization of soybean oligosaccharides extract from sweet slurry by conventional electrodialysis. *Journal of Food Engineering*. 95, 410-415.