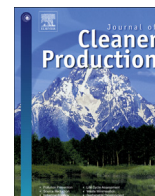




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Closing the loop in the electroplating industry by electro dialysis

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ABSTRACT

The electro dialysis had been already applied for metals recovery in plating processes, however, according to the operational settings, this technology may present loss of efficiency. The aim of this work consists on determine the electro dialysis operational parameters necessary to scale up the process and to close the loop in the nickel electroplating industry. The evaluation in bench scale using synthetic effluents allowed determinations about limiting current density, stack configuration and desired characteristics for the solutions produced by electro dialysis. The parameters defined in these tests were applied in an industrial-scale electro dialysis, in a continuous treatment process connected to an industrial rinse water line of nickel plating. The operation in industrial scale confirmed that the obtained solutions have enough quality to be reuse in the nickel plating process. The reuse of concentrated stream allowed chemicals saving around 20% for nickel plating bath. The diluted solution reached conditions similar to tap water; this characteristic allowed the reuse of this solution as rinse water, reducing 90% the volume of effluent sent to the wastewater treatment plant. The reused solutions did not bring harm to the visual quality of the deposit and its protective properties. With near zero pollutants emissions, electro dialysis treatment may be of significant interest to the electroplating industry, providing a closed loop galvanic process, reducing environmental and economic burdens.

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1. Introduction

Brazil has a privileged world position related to water resources availability. However there is a big variation according to Brazilian regions and to water flow period. Studies and analysis published by Water National Agency (ANA, 2014) indicated the occurrence of high vulnerability related to the water supply, both in terms of the quantity as well as the quality of the hydric resources.

In the South of Brazil, the Sinos Hydrographic Basin – where the present work was done – has 1.6 million inhabitants. In addition to the disposal of industrial effluents from different processes, such as tanneries, surface treatment, metal-mechanic, etc., there is also a great urban sewage discharge (Rodrigues et al., 2008).

Surface treatment processes include metal plating operations, which are one of the major water intensive industries. The

industrial wastewater contains various types of harmful heavy metals and toxic substances such as chromium, nickel, copper, zinc, cyanide and degreasing solvents (Akbal and Camci, 2011). Nickel plating improves the corrosion resistance of the metallic materials as well as provides decorative characteristics (Schario, 2007). The most widely used process is the Watts' Nickel, composed by nickel chloride (NiCl₂), nickel sulphate (NiSO₄) and boric acid (H₃BO₃) and organic compounds that are added in order to improve the characteristics of the surface finishing (Schario, 2007). This process generates wastewater with nickel salts and organic additives that must be treated.

Conventional effluent treatment aims to meet the threshold criteria for wastewater emission by chemical processes such as chemical precipitation. Therefore, this technology generates galvanic sludge, a hazardous waste rich in metals, discharged in industrial landfills (Pozdniakova et al., 2016). In addition, the treated effluent rarely is able to be reused in the plating process as rinse water again. Therefore, new technologies need to be applied to treat effluents and to the recovery of water and chemicals.

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With the ever increasing standard of drinking water quality and the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have gained their importance worldwide during the past three decades. There are companies supplying facilities for metal recovery, for treating drinking water or industrial water, treating wastewater from tannery, electroplating, textile processing, etc (Chen, 2004). Electrochemical technologies have reached a state that they are not only comparable with other technologies in terms of cost but also can be more efficient and more compact (Misra and Rao, 2016).

Electrodialysis (ED) is one of the most recent hydrometallurgical technologies adopted for treat effluents and to the recovery of materials and water. ED is an electrically driven process based on the selective migration of aqueous ions through ion-exchange membranes (Solt, 1971). Treating rinse water by electrodialysis generates two new solutions: one concentrated on ions and another consisting of almost pure water. Both are able to be reused in the plating process (Zoppas-Ferreira, 2014). This technique not only concentrates metals from rinse water, but also helps to maintain the quality of a plating bath (Rodrigues et al., 2008).

Many studies have been conducted with real and synthetic wastewater in order to apply ED for nickel removal from the rinsing water to recover the bath components and to reuse as much water as possible. Bench scale tests was performed in order to evaluate the ED efficiency in the treatment of synthetic and real nickel plating rinse water and assessed the solutions produced by ED for reuse, and also, the quality of the pieces plated and rinsed with these solutions (Benvenuti et al., 2014a). In the same group, bench scale studies was performed about extraction of metals in plating solutions and the effects of operational parameters on the ED results (Bernardes et al., 2000). The removal of nickel using electro-deionization was evaluated in bench scale and related costs was estimated (Dzyazko and Belyakov, 2004). Tests performed in laboratory and in a pilot plant of a galvanic industry evaluated the treatment of a nickel rinse water (5 ppm Ni) applying an hybrid ion-exchange/electrodialysis system (Spoor et al., 2002). Previous studies utilized an ED system with three compartments for treat real nickel plating rinse water and for concentrate nickel into the nickel bath (Tison and Mikhail, 1982; Trivedi and Prober, 1972).

Considering the treatment of dilute solutions, high electrical resistances and the development of the concentration polarization phenomena can limit the economic viability of this technique (Wen et al., 1996). Limiting current density (LCD) is an important parameter for ensure an optimum result, avoiding some problems related to ions transport through the membranes (Marder and Perez-Herranz, 2014).

In this paper, in order to evaluate the efficiency of a continuous ED treatment, additionally to the bench scale test, a full-scale test was performed during a month in a metallurgical industry in the South of Brazil, aiming the recovery of water and chemicals for reuse. Using the data obtained during ED operation, the performances, economic and environmental benefits of ED process were analyzed.

2. Materials and methods

The work was carried out in two different set-up: bench and industrial scale.

2.1. Bench scale system for ED

A synthetic solution based on the composition of a real bright nickel plating rinse water was treated by electrodialysis on a bench scale system. The synthetic solution was made using NiSO_4 , NiCl_2 and H_3BO_3 salts analytical grade and commercial organic additives, featuring 1.3 g L^{-1} Ni, organic matter (27 mg TOC.L^{-1}), conductivity of 3 mScm^{-1} and pH around 4.

The ED bench cell contained 5 compartments and 3 solution reservoirs and was used to obtain two reusable solutions: one concentrated (CS) and another, diluted (DS), as shown in Fig. 1.

The nickel synthetic solution (called effluent) was added to the dilute and concentrated reservoirs (CS and DS) at the beginning of the test. The rinse electrode solution contained 4 g L^{-1} of sodium sulphate and has a conductivity of 5.4 mS cm^{-1} .

All reservoirs (ES, CS and DS) contain 0.5 L of each solution, and each one was connected to a pump for the solutions recirculation (80 L h^{-1}). In both cell ends were placed the electrodes – cathode (Cat) and anode (An), both 16 cm^2 Ti plate coated with $\text{Ti}_{0.7}/\text{Ru}_{0.3}\text{O}_2$.

Hydrochloric acid PA (36%) was used for pH adjustment during the ED treatment (in order to maintain the pH of diluted and concentrated solutions, avoiding the nickel hydroxide precipitation).

Ion exchange membranes – cationic (Ionac MC-3470) and anionic (Ionac MA-3475) – with 16 cm^2 surface area were used. The lifespan of membranes for ED treatment has been showed, in practical applications, ranges from 5 to 8 years (Strathmann, 2010).

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) (Fig. 1); the stack configuration was (Cat) A-C-A-A (-An) and it was adopted to protect the anode, reducing the Ni transport to the electrodes solution, what was reported in previous publications (Benvenuti et al., 2014b).

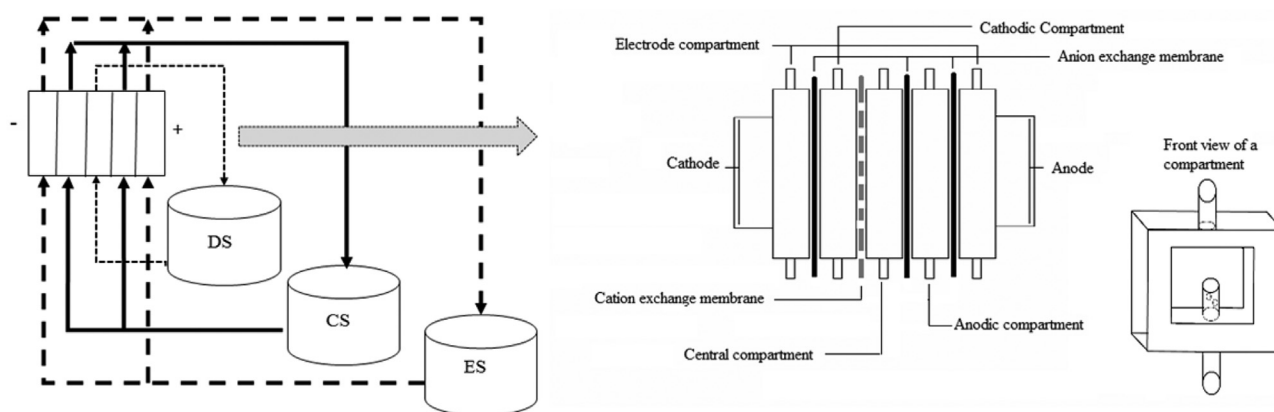


Fig. 1. Electrodialysis bench system used for treat Ni solutions. Electrodes solution (ES, Na_2SO_4), concentrated solution (CS), and dilute solution (DS, effluent). On the right side, the ED stack and its compartments are highlighted.

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