



Treatment of wastewaters from cyanide-free plating process by electro dialysis



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ABSTRACT

Cyanidric compounds are used in certain stages of electroplating processes. However, the toxicity of the cyanide stimulates the development of alternative raw materials. Therefore, the utilization of cyanide-free compounds requires the consolidation of treatment methodologies for this novel type of wastewater generated. One of the alternatives that is currently available consists of the replacement of the cyanide by 1-hydroxyethane 1,1-diphosphonic acid (HEDP). In this study it was employed an HEDP based electrolyte, which was used to produce solutions that simulate the rinse waters of copper strike baths. The application of electro dialysis (ED) in a closed system was evaluated by considering the recovery of the copper, the HEDP and the water. The trials were carried out in an ED cell which contains five compartments. The results showed the extraction of up to 99.7% of the copper and up to 94.4% of the HEDP from the working solution. By varying the pH values, along with the construction of speciation diagrams, it was achieved a separation of the Cu(II)-HEDP complexes. While the characteristics of the treated solutions enabled their reutilization in the rinse tanks, the concentrated solutions can be reused in the electrolyte in order to replace ions lost by drag-out.

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1. Introduction

A common application of copper in electroplating processes is as an intermediate layer in systems of two or more coatings, which increases other metals adherence to the substrates, facilitates polishing of parts and improves the substrate corrosion resistance. Moreover, the addition of cyanide to alkaline copper baths, called strike baths, are used industrially to form complexes with copper, reducing its equilibrium potential and enabling an adhesive layer to be deposited on less-noble substrates than copper (Panossian, 1993).

The attractive cost, uniformity and adhesion of the deposit, coupled with the utilization of relatively simple equipment boosted the use of cyanide based raw materials for many years. In addition to this, the technologies for process control and treatment of wastewater are already well known and widely used among the majority of companies (Piccinini et al., 2000). However, cyanide

salts are linked to the chemical risks that are involved in any electroplating operation, in addition to representing an important type of pollution of natural resources (Dash et al., 2009). Therefore, cyanide toxicity rised the need to replace it by other raw materials that are equally competitive in terms of costs and quality.

One study (Vargas, 2008) evaluated the modification of cyanide-free commercial bath for copper-plating processes on Zamak substrates using a bath based on based on 1-hydroxyethane 1,1-diphosphonic acid (HEDP), which is an organic phosphonate capable of forming stables complexes with metallic ions. This study led to the determination of the operational parameters and formulation of baths for obtaining deposits with a comparable level of adherence and shine to that produced by cyanide based baths, as shown in Table 1 (Vargas, 2008).

Due to its chelating properties, HEDP has industrial applications as a corrosion inhibitor and antioxidant, in treatments of bone diseases, in cleaning agents and in treatment of water in cooling systems (Nowack, 2003; Fischer, 1993). The diversity of applications of HEDP promoted research (Nowack, 2003; Fischer, 1993; Knepper, 2003; Jaworska et al., 2002) on the use of this substance in natural environments. According to Steber and Wierich, 1986 one

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Table 1
Operating parameters and composition of the HEDP based bath (Vargas, 2008).

Cu ⁺² ions	4.5 g L ⁻¹
HEDP	105 g L ⁻¹
Potassium chloride	4 a 10 g L ⁻¹
Salicyl sulphonic acid (optional)	4 g L ⁻¹
Potassium sulfate (optional)	4 g L ⁻¹
pH	10
Density of current applied	From 0.2 to 0.5 A dm ⁻²
Temperature of the bath	From 25 to 60 °C
Agitation	Present

characteristic of HEDP is its photodegradability in sunlight wavelengths, giving rise to acetate and orthophosphate byproducts. Photodegradation of HEDP in the presence of metals was analyzed by Fischer (Fischer, 1993) and the results indicated that the presence of Cu²⁺ ions increased the oxidation of HEDP by 199% (Fischer, 1993).

In electroplating operations, the diluted wastewater produced by the washing of the parts accounts for the greatest consumption of water, which calls attention for the development of methods to recover and recycle most of the water used in such processes (Mclay and Reinhard, 2002). The immersion of parts in one or more water tanks results in the dilution of substances carried from a previous bath, minimizing the contamination of the next process. As a consequence, the concentration of contaminants in rinse waters increases gradually over time due to the drag-out (Evans et al., 2009). Conventional wastewater treatments containing cyanide use oxidizing agents to convert it into a less toxic form, namely cyanate (CNO⁻). The stages that follow the cyanide oxidation are wastewater neutralization and formation of insoluble hydroxides followed by flocculation and precipitation reactions, which results in the production of galvanic sludge (Roy, 1996). The replacement of cyanide by HEDP gives rise to changes in the composition of the effluents produced.

In order to make HEDP based compounds technically and economically viable, it is necessary to consolidate a methodology for treatment of wastewater, recovery of the components and reutilization of the water in the industrial flow.

Electrodialysis (ED) has been explored in the treatment of wastewater resulting from electroplating operations. Electrodialysis (ED) is a membrane separation process which uses an electric potential difference as the driving force to promote ionic transport from different solutions. Semi-permeable anionic and cationic membranes are set correspondingly between two poles – cathode and anode – forming individual compartments, as shown in Fig. 1 (Strathmann, 2004).

Its attraction lies in the possibility of recovery of the water and of the ions contained therein, without any need for phase changes or addition of extra components for oxidative processes (Rodrigues et al., 2007). This technique was developed for desalination of brackish waters and for separation and concentration of acids and salts from aqueous solutions. Nevertheless, modifications in classic procedures of electrodialysis allowed its use in a new range of applications, such as treatment of industrial wastewaters (Strathmann, 2004). The application of ED was evaluated for the treatment of rinse waters from plating processes of metals such as nickel (Benvenuti et al., 2014), cadmium (Marder et al., 2003) and chromium (Nataraj et al., 2007). Studies were developed involving the application of the ED (Chiappello and Gal, 1992; Zuoa et al., 2008; Cifuentes et al., 2009), or ED along with electro-recovery (Peng et al., 2011) or ionic exchange processes (Mahmoud and Hoadley, 2012) for copper recovery.

The formation of complexes between metals and chelating agents in ED processes has been studied. The separation between

nickel and cobalt by the addition of EDTA has been examined, aiming at the formation of stable anionic complexes between EDTA and nickel (Chaudhary et al., 2000). The same principle was used to study the transport of silver, zinc and copper cations with EDTA, assessing the selective separation of silver (Cherif et al., 1993). Moreover, the selective separation capacity of nickel and copper by the chelating agents oxalic acid and glycine were studied (Huang et al., 1988).

However, there are a number of problems associated with the presence of complexes in solution in ED because it may alter the ionic transport in solutions and affect the properties of membranes (Aouad et al., 1999). It was noted that the low mobility of complexes reduces the current efficiency of ion transport (Cherif et al., 1993). In addition, the presence of complexes can increase the resistance of the membranes. Complexes located in the interior of the matrix can result in interactions with sites of the membrane and alter its permselectivity (Aouad et al., 1999, 1997).

In a previous study (Aouad et al., 1997), the transport of Cl⁻ by an anionic exchange membrane (AEM) was reduced in the presence of zinc complexes, while the flow of Na⁺ cations was increased, suggesting that complexes of a certain type neutralize part of the fixed sites of the membrane. The rate of complexes in relation to the free ions is important for transport through membranes, as well as the concentration of the species and the pH values of the solution (Huang et al., 1988; Aouad et al., 1999, 1997).

Industrial application of electrodialysis are related to operational costs of the process, specially the energy consumption. The total energy consumption of the system is usually defined as function of the characteristics of every application. An important parcel of the energy is used to transport the ions through the solutions and the membranes. It is also important to highlight that, in practice, hundreds of membranes pairs can be settled between the electrode compartments (Strathmann, 1995).

The fraction of the current that is effectively used to separate the ion of interest is called current efficiency. The current efficiency (ϕ) is related to the imposed current to the system through the Equation (1) and it is directly proportional to the concentration of ions in the central compartment (Martí-Calatayud et al., 2014).

$$\phi(t) = \frac{n \cdot F \cdot V \cdot (C_t - C_0)}{\int_0^t I dt} \times 100 \quad (1)$$

Through the applied potential between poles, it is also possible to estimate the specific energy consumption to transport an ion in a given moment. The specific energy consumption is related to the applied potential and depends on the ion concentration in the diluted compartment and on its molar mass (Equation (2)) (Martí-Calatayud et al., 2014).

$$E(t) = \frac{\int_0^t U(t) \cdot I dt}{3600 \cdot M \cdot V \cdot (C_t - C_0)} \quad (2)$$

In this study, it was employed the electrolyte described in Table 1 to produce synthetic solutions that simulate the rinse waters of HEDP-based strike baths. The aim of this study was to evaluate the application of ED for copper, HEDP and water recovery. The influence of the type of trial (galvanostatic and potentiostatic) and pH values in the percentage extraction of ions from the wastewater were analyzed. The ionic transport in presence of Cu(II)-HEDP complexes was assessed. The chemical characteristics of the diluted and concentrated solutions generated as a result of the ED process were determined. Due to photodegradation

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