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HIGHLIGHTS

- Electrodialysis can be a cleaner production concept for electroplating industry.
- The main concern about cleaner production is related to water treatment.
- Electrodialysis can be applied to promote water recycling and chemical recovery.
- Future challenges are to improve systems’ efficiency and to reduce operating costs.
- Hybrid systems seem to be the main future applications.
A review of cleaner production in electroplating industries using electrodialysis

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ABSTRACT

Cleaner production is an industrial preventive strategy created to promote benefits for the environment and for human beings. Its basic principle lies in using natural energy resources in an efficient way and yet in reducing risks and impacts on the environment and on human beings throughout the life cycle of a product. Electrodialysis is a membrane separation process which uses an electrical potential difference as a driving force to promote ionic separation in aqueous solutions. The technique was initially developed for the production of drinking water from brackish water. However, the use of electrodialysis in the treatment of industrial wastewaters is becoming more attractive, due to its characteristics. The technique is considered a clean process, since it allows the reuse of water and the recovery of substances. In this work, the advancement of electrodialysis applied to cleaner production in electroplating industry will be discussed. The aim of this work is to present electrodialysis as a technology which can fulfill the requirements of cleaner production concepts in the electroplating industry. The research was performed starting from a predefined question: “how is electrodialysis becoming a cleaner production strategy in the electroplating industry?”. The research was divided in two main themes. The first search was related to the most important cleaner production practices applied for the plating industry. The second search was associated with the electrodialysis application in the electroplating industry. The results obtained from the collected publications were compared in order to propose an answer to the research question. The results showed that almost a half of the published articles evaluated the improvement of the wastewater treatment as a cleaner production strategy to be applied in plating industries. In addition, the wastewater treatment was the most cited application of electrodialysis in the plating industry, especially for copper, nickel and zinc recovery and for chromium VI removal. Results shows that electrodialysis is becoming an
important and solid strategy to promote cleaner production in the plating industry. The two most important issues to be improved for this application are the system efficiency for macromolecules and the energy waste when dilute solutions are used. For the latter, the use of hybrid techniques such as electrodeionization was the most evaluated alternative.

Keywords: electrodialysis; cleaner production; electroplating; wastewater treatment.

1. INTRODUCTION

The cleaner production concept is related to a preventive strategy applied to manufactured products aiming at obtaining a range of benefits for the environment and for human beings. Cleaner production fundamentals are based on improving the efficiency of natural resources and energy utilization, reducing risks for the environment and for human life and also reducing the environmental impact caused by manufactured products throughout their life cycle (Severo et al., 2014; Silvestre and Neto, 2014). Industrial cleaner production practices include, e.g., avoiding or minimizing raw material wastes and energy losses, reducing or eliminating the use of toxic substances and toxic waste emission and promoting recycling and reusing of inputs (Almeida et al., 2013). Cleaner production is multidisciplinary and generic strategies, so that each industry sector can define practical actions in order to achieve their own goals.

The main motivation of this work is the concern about the future scarcity of natural resources faced by the world. One of the main challenges of our civilization is to find balance between economic growth and a cleaner environment (Khalili et al., 2015). The depletion of nonrenewable sources has already begun to modify human activities, such as mining, electric energy generation and fuel production. One important example is copper mining. In the beginning of the 20th century, copper ores contained about 4% of copper. However, the decrease of natural deposits had led mining companies to exploit ores containing less copper. About a century later, the copper concentration in the ores was near 1%. Considering the production and the consumption in the past decades, it is estimated that the copper demand will exceed the supply if
the current situation is maintained (Veit, 2005). Future projects for the activation of new copper mines remain stagnant due to environmental, financial and technological issues.

Nickel mining is another example of a mining process which is threatened by global demand. It is estimated that nickel sulfide ores may be depleted earlier than nickel lateritic ores because they present an easier beneficiation route. However, lateritic ores contain higher amounts of nickel. In the future, it is possible that nickel mining will be carried out mostly from lateritic ores which would affect the nickel price per ton (Mudd, 2010).

The mentioned scenarios have stimulated the development of new approaches for metal extraction. Research is being made to apply mining techniques for metal extraction from waste electrical and electronic equipment as secondary beneficiation routes (Bernardes et al., 2004; Provazi et al., 2011; Silvas et al., 2015; Yamane et al., 2011).

This work focuses on the electroplating industry which is responsible for water and metal consumption. The treatment of electroplating waste was discussed several times during the past decades. Waste from electroplating and other metal finishing operations is considered hazardous and may represent a loss of raw materials. In order to minimize these effects, membrane separation processes started to be used in metal finishing industries. In this work, a systematic review was performed to discuss the technological advancement of membrane separation processes, especially electrodialysis, applied as a cleaner production tool in the electroplating waste treatment.

1.1 A brief review of electroplating processes

The principles of electroplating began to be used in the eighteenth century. The most accepted hypothesis is that the first deposition of metals was made in 1772 (Raub, 1993). At that time, however, there was not a sufficiently powerful energy supply for the improvement of the technology. Twenty five years later, Alessandro Volta developed the first electric battery, using the principles discovered by Luigi Galvani (Raub, 1993). The new advances allowed Luigi Brunatelli to hold the electrodeposition of gold on silver medals. In 1840, the electrodeposition process was patented and two British brothers,
Henry and George Elkington, started a commercial scale production. They obtained the monopoly of electroplating for years (Bard et al., 2012). Since then, the electroplating process became one of the most important steps of the surface finishing industry.

In the middle of the 1970s, the first laws including the disposal of waste from the electroplating process were written. One of the examples is the Public Law 92-500, Water Pollution Control Amendments, established in 1972 in the United States, to preserve the integrity of local water bodies (Christensen and Delwiche, 1982). The emergence of such laws was related to evidences that industrial discharges contained toxic substances, such as chromium, copper, zinc, nickel, cyanide and other chemical reagents (Christensen and Delwiche, 1982; Rodrigues et al., 2014). If these substances are released to the environment with no proper treatment, they can have toxic effects on the environment, on fauna and flora as on human beings.

It is well known that the conventional electroplating wastewater treatments are flocculation, precipitation and filtration. These processes are still used in plating industries. However, some factors have been contributing to the development of novel technologies. These factors include the increasing severity of environmental laws, the economic issues relating to the waste of raw materials and the need to reuse the water due to global threats of drinking-water scarcity. In recent decades, membrane separation processes have been modified and improved for their use in the treatment of different industrial effluents. Membrane separation processes are mainly used for selective separation and concentration of ions. Their most important attractiveness lies in the fact that they may allow water recycling and the simultaneous recovery of other compounds contained therein.

1.2 Evolution of electrodialysis and the development of ion exchange membranes

Historically, the development of membranes began in the eighteenth century with the conception of the term "osmosis" which means the permeation of water through a diaphragm (Hoek et al., 2013). In 1850, H.P. Thompson and J.T. Way noted the effect of ion exchange in the soil and this fact had driven the
early research on ion exchange membranes (Sata, 2004). During the same period, studies in cell membranes contributed to the synthesis of the first inorganic ion exchange systems. The first processes using ion exchange membranes occurred about forty years later, with the study of W. Ostwald on the properties of semi-permeable membranes (Xu, 2005). It was the first study that proposed that there is a potential difference at the boundary layer between the membrane surface and the electrolyte. In the study of Ostwald, this potential difference was considered as a result of the ion concentration difference between phases (Xu, 2005).

In 1855, Fick postulated the theories of atomic diffusion (Hoek et al., 2013). In 1911, Donnan proved the existence of this potential difference and created the term Donnan exclusion potential or Donnan potential (Strathmann, 1992). As of the 1940s, the studies on ion exchange membranes generated industrial interests. At that time, the first synthetic polymeric membranes began to be manufactured (Strathmann, 1992).

The first mention of the electrodialysis term was used around that same period when an application of dialysis, combined with electrolysis to demineralize sugar syrup using membranes made of permanganate paper, was proposed (Shaposhnik and Kesore, 1997). Nowadays, electrodialysis is defined as a membrane separation process which uses an electric potential difference as a driving force to promote ionic transport from different solutions with the aid of semi-permeable membranes.

In 1954, the Saudi oil company Aramco installed the first electrodialysis system in its industrial park for brackish water desalination. The treated water was used by the company itself (Aly et al., 1989). By the 1970s, electrodialysis was mainly used for brackish water desalination. Since then, the technique has been modified and improved for its use in the industrial wastewater treatment. In 1973, a report of the Environmental Protection Agency, in the United States, investigated the treatment of solutions containing cyanide from an electroplating industry using electrodialysis (Tuwiner, 1973). The timeline of the ion exchange membrane and electrodialysis development is shown in Figure 1.

FIGURE 1
According to Korngold (Korngold et al., 1978), the membrane separation processes were more suitable for wastewater treatment in the 1970s. However, there were some operational issues involving the usage of these processes (Korngold et al., 1978). High ion concentrations in the wastewater could cause membrane clogging. However, low ion concentrations could cause excessive energy consumption. The presence of low-mobility ions also represented a challenge to be overcome (Huang et al., 1983).

In the 1980s, studies were developed for metal recovering from industrial wastewater using electrodialysis (Audinos, 1986; Huang et al., 1983; Rao et al., 1989). The separation and recovery of chromium ions from tannery wastewater was evaluated by Rao et al. (Rao et al., 1989). The transport of copper ions through ion exchange membranes was studied by Huang et al. (Huang et al., 1983) since copper is present in many different industrial wastes. Audinos (Audinos, 1986) studied zinc-ion recovery from electroplating wastewater using electrodialysis. The results presented by the mentioned authors showed that electrodialysis could be used as a subsequent process allowing a water treatment and a metal recovery in the concentrated compartments. Researches also intended to overcome the mentioned operational issues of adapting electrodialysis for industrial wastewater treatments. Therefore, the membrane structural modification or the synthesis of novel membranes were performed to produce more suitable membranes for the new conditions (Chakravorty et al., 1983; Sata and Izuo, 1989). The use of the reverse electrodialysis began to be evaluated as an alternative to prevent the formation of precipitates on membrane surfaces (Fubao, 1985).

A schematic drawing of an electrodialysis system is presented in Figure 2. In an electrodialysis system, an electric potential difference is applied as a driving force to promote the ionic transport from different solutions. Semi-permeable anionic and cationic membranes are set between two poles – cathode and anode – forming individual compartments. As a result, two solutions are formed, one more diluted (water after treatment) and the other, more concentrated (recovered ions) than the original one (Strathmann, 2004). A schematic drawing of an electrodialysis system is presented in Figure 2.
2. RESEARCH METHODS

In this work, a systematic review was performed based on a formulated research question: “How is electrodialysis becoming a cleaner production strategy in the electroplating industry?”. The purpose of this work is to synthesize scientific data that contribute to consolidate electrodialysis as a feasible process aiming at a cleaner and sustainable production in the surface treatment industry.

The research topics were classified in two main categories: the first category is related to the most important cleaner production strategies applied in an electroplating industry and the second one is associated with the application of electrodialysis in an electroplating industry. For each category, the research strategy, the scholarly database, the keywords and the periods of publication were defined.

The research strategy was to search for relevant scientific papers published in scientific journals using one of the most recognized academic database, Scopus, and ScienceDirect website, which provides access to a database of scientific research from Elsevier. Books and conference papers were not considered, although they were used in item 1 (Introduction) to contextualize this work. The research was performed considering the period of publication from 1990 to 2016. The period was chosen based on the International Declaration on Cleaner Production: Implementation Guidelines for Companies (United Nations Environment Programme, 2001) which considers 1989 as the year in which the term “Cleaner Production” was firstly introduced by the United Nations Environment Programme (UNEP).

The following combinations of keywords were used:

i) “cleaner production practice” AND “electroplating industry”;
ii) “cleaner production” AND “electroplating”;
iii) “waste minimization” AND “electroplating”;
iv) “cleaner production strategy” AND “electroplating”;
v) “electrodialysis” AND “electroplating”.

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For both categories defined previously, the same process of search was used. The process is presented in Figure 3.

FIGURE 3

The initial search was performed using the listed combination of keywords. The results were classified according to the two main categories: “cleaner production strategies in electroplating industry” and “electrodialysis application in electroplating industry”. The results were then reviewed and filtered by title and abstract. Duplications in search results were excluded. Also, some criteria were adopted in order to evaluate the most relevant articles to be considered for full text analysis: language, abstract availability, type of article (original article or review). The main concepts of the proposed research, i.e., the cleaner production practices, the electroplating industry or the electrodialysis technique must have been clearly defined in the articles title, abstract or keywords, so that the article could be considered for full text analysis.

After the first filtering process, the remaining articles were fully evaluated. The data were organized by using an electronic spreadsheet. Some statistical analyses were conducted (Morioka and Carvalho, 2016), considering mainly the year of publication, the type of the article (original, review or case study) and the main theme. The main themes were defined by analyzing the key objectives of each article and classifying them in subcategories. Full articles related to the cleaner production practices in electroplating industry were classified according to the following themes:

I. Wastewater treatment: original articles about physical, chemical, thermal or electrochemical techniques used to purify industrial effluents;

II. Policy and regulation: local or international regulations, laws or innovative public policies, regulation for emissions of pollutants;

III. Management tools: articles containing methods for identifying potential improvements, environmental audits, economic assessments, waste management;
IV. Modeling tools: the expression “modeling tools” was used to categorize the studies that were developed using computational methods applied to industrial waste. The application of multiple criteria decision-making, of fuzzy logic models and of graph theory are a few examples of research which were categorized as modeling tools (Kumar and Agrawal, 2009; Kumar et al., 2010; Telukdarie et al., 2005);

V. Process modification: original articles containing practical measures which were used to modify the manufacturing processes and resulted in a more sustainable production flow;

VI. Solid waste recycling: solid waste recycling methods were intentionally separated from effluents because they present different characteristics in comparison with liquid effluents and, thus, they are treated and discarded in separated manners.

Full articles associated with electrodialysis in plating industry were classified as:

I. Wastewater treatment: general application of electrodialysis for wastewater treatment;
II. Metal recovery: evaluation of metal recovery after electrodialysis;
III. Water reclamation: evaluation of the possibility of reusing water after electrodialysis;
IV. Ion transport through membranes: original articles about the transport properties of ions from synthetic electroplating electrolytes through ion-exchange membranes;
V. Membrane development: development of new membranes for electrodialysis applications;
VI. Electrochemical techniques: evaluation of other electrochemical techniques related to electrodialysis, such as electrodeionization or electroelectrodialysis;
VII. Metal removal: metal extraction from plating wastewater using electrodialysis;
VIII. **Hybrid electrodialysis processes**: combination of electrodialysis and one or more techniques, such as filtration, ion exchange resins or photo oxidation;

IX. **Membrane fouling**: studies on membrane clogging applied to electroplating industry;

X. **Chemical recovery**: evaluation of the recovery of chemicals (non-metals), e.g. cyanide;

XI. **Bath purification or regeneration**: removal of contaminants from the plating bath with the aim of increasing bath life.

Finally, the more relevant papers were used to make a final discussion in order to answer the proposed research question.

3. **RESULTS AND DISCUSSION**

3.1 **Cleaner production strategies applied to the electroplating industry**

The evolution of the number of publications related to the cleaner production concepts applied to the electroplating industry since 1990 is shown in Figure 4.

FIGURE 4

From Figure 4, an increase in the number of publications since 2005 is observed. It seems that, in the last decade, the concern about the environmental impacts caused by the electroplating industry has increased. Some relevant facts can be related to this behavior (Machado et al., 2012; Steward et al., 1999):

1. The environmental and occupational legislations have become more rigorous. Global policies are encouraging the sustainable use of natural resources. Throughout the last years, the environmental concern around the world has become more evident. Although the first global conference about environmental issues was held in 1972,
the most famous worldwide meeting is considered to be the “United Nations Conference on Environment and Development (UNCED)” which was held in Rio de Janeiro (Brazil) in 1992 (Penedo et al., 2016). More than 170 global leaders participated in order to discuss the need of a global conscientious change to maintain the environmental life on Earth. However, 10 years later, at the “World Summit on Sustainable Development”, in Johannesburg, very few advances were performed in relation to the commitments assumed in the UNCED. Since then, other global meetings were held in 2007 (United Nations Climate Change Conference), 2009 (United Nations Climate Change Conference), 2011 (United Nations Climate Change Conference) and 2012 (RIO+20). According to the Brazilian government, during the RIO+20 conference, 188 countries agreed to invest US$ 513 billion in projects, partnerships, programs and actions during the following ten years in the areas of transport, green economy, energy, water, environmental protection, climate change and global poverty;

2. The raw material and the waste disposal costs increase every year. Around 2 billion tons of waste are dumped per year and 400 million tons of hazardous waste are produced (The World Counts, 2016);

3. The water consumption per manufactured part in electroplating industries is usually high. It is estimated that 20 % of the total withdrawal of fresh water from nature is directed for industrial use (The World Counts, 2016). It is well known that the water consumption in metal finishing industry is relevant. One example is the research of (Daylan et al., 2013). Authors showed that a single small and medium-size zinc plating plant consumes 2,800 t of water per year which means 1.97 kg of water per dm² of a manufactured piece;

4. The worldwide water crisis created the urgent need for water recycling;

5. The threat of mineral scarcity impels secondary processing routes. It is estimated that, in the near future, the demand for metals will be
supported from mined ores and from recycled metals (Norgate et al., 2007).

The mentioned facts have become more evident in the 21st century and seem to be applicable for practically all industrial sectors. The trend, showed in Figure 4, appears to be in accordance with the environmental concern and it is possible to suggest that, recently, the number of publications is an indicator that the concepts of cleaner production started to be applied to the plating industry in order to minimize the environmental impacts caused by plating processes.

Figure 5 shows the distribution of the published papers related to cleaner production strategies in plating industry which were previously classified in six main themes: wastewater treatment, solid waste recycling, policy and regulation, modeling tools, process modification and management tools.

FIGURE 5

By analyzing Figure 5, it can be seen that 40.19% of the total number of 107 publications was categorized as “wastewater treatment”. The two most important cleaner production strategies, which have been evaluated and published for plating industry application, are the wastewater treatment and the process modification. The latter includes every improvement that can be made in the manufacturing flow in order to achieve a goal that can be considered “cleaner”. Although the definition of “cleaner” is rather generic, it can be related to reducing environmental impacts throughout the life cycle of a given product. Examples are: reduction in water consumption, replacement of toxic raw materials, energy saving and recovery of raw materials.

The research of Giannetti et al. (2008) is an example of interventions that were made in a gold-plated jewelry company in order to achieve a cleaner manufacture. The results of Giannetti et al. (2009) showed a reduction of about 35% of water consumption when a manual-control flow was installed in the rinsing tanks. The water inlet of each rinsing tank started to be opened manually only when the rinsing water achieved a preset turbidity degree. In the same study, the reduction of the electric energy use was evaluated. Polyvinyl chloride (PVC) balls were placed upon plating baths that operate between 65 °C and
90 °C, producing a superficial layer able to control electrolyte evaporation. As a result, the energy saving achieved 18 % after the intervention.

Daylan et al. (2013) applied some process modification in a zinc plating plant. In 2005, the production capacity of the plant was 6,000,000 dm² parts per year and the rinsing water consumption was 10,384 m³/y. One of the interventions in the production flow was the use of a closed loop cleaning system that replaced the conventional pre-treatment rinse system. The authors achieved energy saving, reduced the sludge generated in this step, created a safer environment for workers and recovered the cleaning solution in pre-treatment steps. The following countermeasures were implemented: the rinsing tanks operation was modified to reduce the rinsing water consumption; the number of water inlets was reduced; a reverse osmosis system was coupled with the first rinsing tank; a drag-out tank was installed after zinc plating and the solution was periodically returned to the plating bath; and the rinsing step was modified to operate in counter current rinsing. The authors estimated that the implemented countermeasures could help the industry to save about 4000 € per year, to reduce 88 % of water consumption and 680 kg/y of hazardous raw material consumption.

In the study developed by Chen et al. (1996), the authors suggested that a modification in a chromium plating plant could lead to an environmentally friendly process. According to the authors, the implantation of nitrogen in chromium plating would improve the surface hardness and therefore, there would be a reduction in the chromium thickness which would reduce the amount of a hazardous raw material.

Demirer (2014) reported a case study in a cadmium plating process. A hand wiping degreasing process was replaced by an alternative “cleaner” practice which led to a reduction of almost 93 % in the consumption of the degreasing agent and saved 61 % of the workforce. Two hazardous raw materials were replaced by an environmentally friendly alternative, saving 475 kg of raw materials per month. From this study, a total annual cost saving of US$ 43,372 was estimated. The cost saving is an interesting aspect about cleaner production because it shows that when a company adopts sustainable concepts, the benefits can be reflected in the economic performance.
Munsamy et al. (2014) developed a closed system to implement an evaporative cooler to save the plating bath from evaporative losses and to reduce the waste production.

Alkaya and Demirer (2013) proposed process modifications and management practices to a zinc-phosphating process. The process modifications performed were to place drain boards to recover drag-outs, to apply counter current rinsing and to install covers on top of tanks to prevent evaporation. The main obtained results were the reduction of water consumption in 34%; the reduction of raw material consumption by 1400 kg/year; the reduction of wastewater production by 3200 m³/year; the reduction of sludge production by 4600 kg/year and 36% of energy saving.

The mentioned examples of published process modifications are summarized in Table 1.

TABLE 1

From Figure 5, it is possible to observe that the modeling tools correspond to almost 24% of the researches which indicates that computational tools have become an important strategy, especially after the digital age. About 80% of the papers related to modeling and software tools were published after the year 2000.

As observed previously, 43 papers were categorized as “wastewater treatment”. They were chosen to be the samples of the review for the first main theme (cleaner production practices in plating industry) and they proposed methodologies for water treatment. The main techniques that were evaluated by the authors were: adsorption, biosorption, leaching, solvent extraction, photoelectrooxidation, ion exchange, electrowinning, nanofiltration, ultrafiltration, reverse osmosis, electrodialysis and electrodeionization. A list containing the 43 articles is presented separately in Appendix A.

Considering the 43 articles categorized as “wastewater treatment” and chosen to be the samples of the review, four were highlighted (Frenzel et al., 2005; Lu et al., 2015; Scarazzato et al., 2014; Tran et al., 2015) because they
proposed practical applications of electrodialysis as a feasible wastewater treatment process.

Lu et al. (2015) used a two-stage electrodeionization system to recover \( \text{Ni}^{2+} \) and water from a plating wastewater. The authors achieved 94 % of nickel-ion removal in the first stage and 96.7 % in the second stage, totaling 99.8 % of \( \text{Ni}^{2+} \) extraction. The concentrated solution contained 11 g/L of \( \text{Ni}^{2+} \) which represents a concentration about 220 times higher than the wastewater in its initial stage. The produced water presented a resistivity of 1.6 MΩ. The total treatment capacity was estimated at 1.0 m³/h. The authors reported that the wastewater treatment using electrodeionization was able to reduce wastewater discharge in 7200 m³/year and the sludge disposal in 12.8 t/year.

The application of electrodialysis was evaluated for treating a simulated wastewater from a cyanide-free copper plating bath (Scarazzato et al., 2014). A five-compartment laboratory-scale system was used in order to recover copper ions and 1-hydroxyethane,1,1-diphosphonic acid (HEDP) from a synthetic solution. The authors obtained 99.7 % of copper extraction and 94.4 % of HEDP removal in one-stage experiments. The highest desalination rate achieved was 87.5 % which means that the resistivity of the water produced was 5.2 kΩ. The results indicated that electrodialysis was suitable for the mentioned process and contributed to enabling the replacement of cyanide in the strike copper bath.

Tran et al. (2015) evaluated a hybrid system that combined crystallization and electrodialysis using bipolar membranes aiming at removing calcium and nickel ions from a nickel plating process. The evaluated wastewater contained the following cations: calcium, nickel, sodium, strontium, iron and chromium, apart from sulfate anions. The wastewater was pretreated in a fluidized pellet reactor in order to avoid calcium ion and nickel ion precipitation in the base compartment. After the pre-treatment, the solution was used to feed an electrodialysis system which operated with monopolar and bipolar membranes. The objective of bipolar electrodialysis was the simultaneous regeneration of acid and base. As results, a 1.76 mol/L acid solution and a 2.41 mol/L base solution were obtained after a 6 h test. According to the authors, the production of acid and base solutions by means of bipolar electrodialysis is an environmental friendly process since the acid/base product can be used for, e.g., steel pickling and other plating plants.
An electro-electrodialysis system for chromic acid recovery was evaluated by Frenzel et al. (2005). The authors studied the stability of anion-exchange membranes against oxidative solutions. Three membranes were investigated for chromic acid recovery in a three-compartment test cell. Two effluents (one synthetic and one industrial) containing chromium ions were used as feed solutions. The authors established the optimal conditions for a further up-scaling of the process and determined the current efficiency and the energy consumption for each membrane. According to the authors, the Fumasep® FAP anion-exchange membrane was found to be the most efficient in chromic acid recovery with an overall current efficiency of 0.14 for CrO$_3$ and an energy consumption of 1.6 kW.h per mol of CrO$_3$. The chromic acid recovering process requires a current density range of (10-20) mA/cm$^2$, temperature between 40 °C and 50 °C and a flow rate equal to or higher than 7 cm/s.

### 3.2 Electrodialysis applied to the electroplating industry

Figure 6 shows the evolution of publications related to the electrodialysis application in plating industry. As of 2008, it is noted that the number of publications increased. Although electrodialysis was developed more than 50 years ago, its use in plating industry can be considered relatively recent.

**FIGURE 6**

As it was showed in Figure 3, the samples of the review totalized 55 publications which were classified by considering the 11 keywords listed in Section 2, chosen after the evaluation of the paper’s main theme. A list detailing the 55 publications is presented in Appendix A. One single paper could be classified in more than one category, according to the objectives of the research. The results are presented in Figure 7.

**FIGURE 7**
The results presented in Figure 7 show that the three most relevant topics of the application of electrodialysis in the plating industry are wastewater treatment, metal removal and metal recovery. It was seen that 37 studies had clearly defined that the application of electrodialysis in the plating industry was related to the wastewater treatment. It is possible to observe that 24 articles intended to recover valuable metals from the wastewater, 8 proposed chemical (non-metal) recovery and 11 evaluated water recycling. These numbers reflect the concern about the scarcity of non-renewable resources.

It is important to note that the application of hybrid systems is becoming important to improve the efficiency of electrodialysis. Sadyraeva (2016) studied a liquid membrane-electrodialysis process to remove hexavalent chromium from synthetic solutions. After a 4 h test, Sadyraeva achieved a complete removal of chromium and a desalination rate of 90%. Dermentzis (2010) removed 83% of nickel ions from a simulated plating wastewater after 35 min using an electrostatic shielding electrodialysis. Lu et al. (2015) evaluated a two-stage electrodeionization process to remove almost 100% of nickel ions from a simulated nickel-plating wastewater.

A special focus should be given to the electrodeionization technique which was one of the most cited hybrid methodologies. Almost a half of the 11 papers evaluated electrodeionization as a hybrid technique and all of them obtained a percent extraction of over 97% of the ions of interest (Alvarado et al., 2013; Dermentzis, 2010; Lu et al., 2015, 2014; Spoor et al., 2002). Electrodeionization is a novel hybrid technology which combines electrodialysis and ion exchange resins in order to achieve a synergic combination of the advantages presented by both methods (Zhang and Chen, 2016). In an electrodeionization system, ion exchange membranes are arranged similarly to an ordinary electrodialysis stack. Inside the diluted compartment, an ion exchange resin bed is inserted. The ion exchange resin improves ion transfer, especially when low conductivity solutions are used. The water dissociation inside the cell generates H⁺ and OH⁻ ions that promote simultaneous resin regeneration (Alvarado and Chen, 2014).

As it was mentioned before, almost a half of the 55 publications were related to metal recovery showing a greater concern about saving raw
materials. From the results presented in Figure 8, it can be seen that the most recovered metals were nickel, copper and chromium, followed by zinc.

**FIGURE 8**

The concern about the availability of copper and nickel ores has been discussed previously in Section 1. It is estimated that the active copper ores could be depleted in about 30 years (Veit, 2005) and the beneficiation of sulphide nickel ores will be replaced by lateritic ores (Mudd, 2010).

Another important fact is that zinc, copper and nickel are among the most common metals used in plating industries. The Watts nickel bath is the most used commercial nickel plating bath, however two other important ones are nickel fluoborate baths and electroless nickel plating baths (Dennis and Such, 1993).

Copper plating is a versatile process, mainly because copper can be plated in a variety of substrates by means of acid baths, alkaline baths and electroless processes. The most known copper electrolytes are the strike alkaline baths, the fluoborate acid baths and the sulfate acid baths. However, the most common applications are the cyanide alkaline strike baths and the sulfate acid bath (ASM Specialty Handbook, 2001). Table 2 presents typical compositions of a Watt nickel bath and copper acid and alkaline baths.

**TABLE 2**

Some interesting facts about plated manufactured were taken from the work of Castelblanque and Salimbeni (2004). About 3000 items of one single car are electroplated. In an airplane, the number of electroplated parts can achieve 2 million. Besides, Western Europe electroplating industries are responsible for the generation of about 1% of the solid and liquid wastes in the region. These data can provide an estimative about the amount of metal salts that are used by plating industries daily over the world.

**3.3 Challenges to overcome and future possibilities**
The application of electrodialysis in the treatment of industrial wastewater has been extensively carried out. Nevertheless, there are many challenges to be overcome. Some industrial wastes containing organic molecules or macromolecules still present low efficiency in electrodialysis stacks and, sometimes, cause a reduction of membrane operational life due to fouling or scaling (Nikonenko et al., 2014). According to Sata (2004), an ion exchange membrane which operates in sea water concentration processes may present a lifespan of about 10 years. This time could be reduced to half in operations in which the current density applied is 10 times higher. The membrane lifespan may be even smaller when in contact with oxidizing agents or extremely acid or alkaline solutions (Sata, 2004). Wastewaters from plating industry may contain large molecules from organic additives used in some baths. In this case, the feasibility of electrodialysis should be thoroughly evaluated before the implementation of a process. If the molecules are too large, the possibility of fouling in anion exchange membranes is enhanced and the system efficiency may be negatively affected. One possibility is to add a pre-treatment step in order to remove the organic substances (Tanaka, 2007). Recently, special membranes have been developed to improve the selectivity for small and medium organic anions. These membranes have shown to be suitable for arsenate-containing species (Pessoa-Lopes et al., 2016) and for fumaric acid (116 g.mol$^{-1}$) (Prochaska and Woźniak-Budych, 2014) recovery. Electrodialysis reversal may be an efficient alternative for preventing fouling caused by large anions. It consists in a periodical inversion of the electric field to reduce fouling and thus achieving high water recovery (Bouhldel and Rumeau, 2004). On the other hand, the use of electrodialysis reversal must be evaluated for each system since it can promote the formation of insoluble compounds (Lu et al., 2014) instead of preventing fouling. Organic and inorganic fouling may also be prevented by using chemical cleaning of ion exchange membranes (Guo et al., 2015; Lee et al., 2008). Surface modification of anionic membranes may improve their anti-fouling characteristics by changing the surface charge or the hydrophilicity of exchange groups (Grebenyuk et al., 1998; Mikhaylin and Bazinet, 2016).

Because of the future challenges concerning the lack of potable water in the world (Gorjian and Ghobadian, 2015), electrodialysis is becoming more
attractive as a seawater pre-desalination process (Galama et al., 2014). Moreover, attention has been given to the cost minimization of electrodialysis (Nikonenko et al., 2014; McGovern et al., 2014). The cost issue is an important step to increase the utilization of electrodialysis in industrial scale, so that, in the future, water can become more accessible to the global population with no depletion of natural resources. Nayar et al. (2016) proposed a feasibility study for in-home water desalination in India. Authors reported that a reverse osmosis system was being used, but it presented a low recovering rate (about 25%). The proposed small-scale electrodialysis system presented a very competitive cost in comparison with reverse osmosis and a water recovery rate of 80%. McGovern et al. (2014) evaluated a hybrid ED-RO system and reported that electrodialysis can be more effective in water recovering than reverse osmosis with a competitive cost. An increase of costs in an electrodialysis stack would depend mostly of the salinity of the feed solution, as stated by the same authors in other study.

In the electroplating field, the treatment of dilute solutions must be taken into account. Low concentrations may raise energy consumption and cause concentration polarization (Benvenuti et al., 2016). In the economic assessment developed by McGovern et al. (2014b), authors reported that the cost effectiveness of electrodialysis strongly depends on the ratio between the salinities of concentrated and dilute solutions. The costs issue is a fundamental point to determine the feasibility of ED for the treatment of plating wastewater and should be thoroughly evaluated before the implementation of the process. It is very difficult to estimate the total cost of an electrodialysis process since it depends on the volume of treated wastewater. In addition, there are costs related to investment, maintenance, piping and personal that difficult a simple estimative of the total cost of electrodialysis implementation. However, in the study of Benvenuti et al. (2016), for example, the cost savings after implementing an electrodialysis stack for treating a real wastewater from a nickel plating process was estimated in 5,000 US$/year.

The presence of diluted solutions in an electrodialysis stack for wastewater treatment is one of the most important reasons for the increase in the number of researches on electrodeionization. The use of ion exchange resin in the diluate compartment may form a preferential path for ions and, as
consequences; a decrease in the electrical resistance and in energy consumption may be achieved. Another recent development to overcome the low salinity issue is the operation of electrodialysis systems in overlimiting regimes (Lu et al., 2010; Nikonenko et al., 2014). According to authors, overlimiting regimes are suitable for electrodeionization systems when water splitting is enhanced, since the water splitting products may favor the regeneration of ion exchange resins. On the other hand, overlimiting governed by electroconvection mechanism may be an alternative for electrodialysis systems in order to increase mass transfer from the bulk towards the membrane-solution interface (Urtenov et al., 2013).

4. CONCLUSIONS

The aim of this work was to present a historical review of the electrodialysis technique and contextualize its use within the industrial practices of cleaner production. The application of electrodialysis in the treatment of electroplating wastewater can support the wastewater treatment, by promoting water reclamation, raw materials recovery and an extension of bath operational life, since the concentrated solutions can be reinserted in the bath tanks. Moreover, it can be an effective measure to waste minimization and to raw material consumption reduction.

In order to contextualize electrodialysis within the electroplating industry, an extensive research was performed including to main questions to be answered: “what are the main cleaner production strategies adopted by plating industry?” and “what are the possible applications of electrodialysis in the electroplating industry?”. As results, 1907 articles were found and filtered according to the criteria: language, availability, type of article, adequacy to the proposed theme. After full text analysis and categorization, 98 articles were used as samples of the systematic review.

The results showed that the most studied practice for implementing cleaner production in electroplating industries is the wastewater treatment. About 40% of the analyzed articles were related to the mentioned theme. At the same time, 37 of 55 articles about electrodialysis in plating industry had the
objective of promoting wastewater treatment, followed by metal recovery and water reclamation. In addition, it was observed that nickel, copper, chromium and zinc are the metals with higher interest to be recovered or removed from the wastewaters. In the case of chromium, this fact is related to the toxicity of its hexavalent form, Cr(VI). In the case of zinc, copper and nickel, the greater interest lies in metal recovery to save raw materials. These relation shows that electrodialysis is being evaluated as a cleaner production strategy that can be applied to wastewater treatment, removing metals and other chemicals and promoting water recycling.

Attention should be given to the researches on hybrid systems, especially electrodeionization technique, which is composed of an electrodialysis stack operating along with ion exchange resins. This is a suitable method especially for treating diluted wastewater, such as the rinsing waters from electroplating baths. One of the most important challenges to overcome is the cost issue, which is directly related to the salinity of the solutions. The development of researches on electrodeionization may reduce the costs related to energy consumption. Another important fact is the improvement of the system efficiency when solutions containing macromolecules are utilized, in order to extend the operational life of membranes. This is particularly important to avoid membrane clogging. The development of modified membranes and the use of electrodialysis reversal can be useful tools to enhance the membrane lifespan in these situations.

APPENDIX A

5. ACKNOWLEDGEMENTS

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96, 30–43. doi:10.1016/j.jclepro.2014.01.099


Kumar, A., Agrawal, V.P., 2009. Expert Systems with Applications Attribute based specification, comparison and selection of electroplating system using


Martí-Calatayud, M.C., García-Gabalondo, M., Pérez-Herranz, V., 2012. Study of the effects of the applied current regime and the concentration of chromic acid


The World Counts, 2016, Copenhagen, Denmark (www.theworldcounts.com)


## APPENDIX A

<table>
<thead>
<tr>
<th>Topic/Category</th>
<th>Number of Articles</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaner production strategies applied to the electroplating industry / Wastewater treatment</td>
<td>43</td>
<td>(Abou-elela et al., 2008; Abou-Elela et al., 1998; Agrawal and Sahu, 2009; Álvarez-Ayuso et al., 2007, 2003; Benvenuti et al., 2015, 2012; Carrillo-Abad et al., 2012, 2011; Chai et al., 1997; Chang, 1995; Diban et al., 2011; Duprey et al., 2014; Eyupoglu et al., 2015; Frenzel et al., 2006, 2005; García et al., 2013; Grebenyuk et al., 1996; Heller et al., 1998; Kuchar et al., 2006a, 2006b; Kul and Oskay, 2015; Kurniawan et al., 2006; Li et al., 2010, 2014; Liu et al., 2016; Lu et al., 2015; Martín-Lara et al., 2014; Mohamma et al., 2004; Morgan and Lee, 1997; Patil, 2012; Petrinic et al., 2015; Philipp, 1995; Saeid et al., 2016; Sankararamakrishnan et al., 2008; Scarazzato et al., 2014; Silva-Martínez and Roy, 2013; Sthiannopkao and Sreesai, 2009; Sze and Xue, 2016; Tran et al., 2015; Vijay and Sihowala, 2002; Weber, 2007; Wong et al., 2003)</td>
</tr>
<tr>
<td>Electrodialysis applied to the electroplating industry</td>
<td>55</td>
<td>(Alvarado et al., 2013; Basha et al., 2008; Benvenuti et al., 2016, 2014; Bergmann et al., 2009; Bolger and Szlag, 2002; Bouhldel and Rumeau, 2004; Caprarescu et al., 2011, 2009, 2015a, 2015b, 2014; Chang et al., 2015; Chekioua and Delimi, 2015; Chen et al., 2009; Chiapello and Galb, 1992; Costa et al., 2002; Cristian et al., 2015; Crotty and Bailey, 2002; Dermentzis, 2010; Dermentzis et al., 2009; Feng et al., 2008; Frenzel et al., 2005; Gayathri and Kumar, 2010; Grebenyuk et al., 1998; Green et al., 2001; Güvenç and Karabacakoglu, 2005; Heller et al., 1998; Jin et al., 2016; Scarazzato et al., 2015;</td>
</tr>
</tbody>
</table>
Khan et al., 2007; Korzenowski et al., 2008; Li et al., 1999; Longfield et al., 2001; Lu et al., 2015, 2014, 2010; Mahmoud and Hoadley, 2012; Marder et al., 2016, 2009, 2004; Martí-Calatayud et al., 2012, 2011; Öğütveren et al., 2016; Paquay et al., 2000; Peng et al., 2011; Pierard et al., 2002; Sadyrbaeva, 2016; Scarazzato et al., 2015; Smith and Foreman, 2016; Spoor et al., 2002; Tran et al., 2015; Wiaux and Nguyen, 1990; Wisniewska and Winnicki, 1991)
<table>
<thead>
<tr>
<th>Process modification</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manual flow control in the rinsing tanks</td>
<td>35% reduction of water volume (Giannetti et al., 2008)</td>
</tr>
<tr>
<td>PVC balls in bath tanks to reduce evaporation and heat losses</td>
<td>18% savings in energy consumption (Giannetti et al., 2008)</td>
</tr>
<tr>
<td>Technology improvement using a closed loop system</td>
<td>Possibility of recovery and reuse of cleaning solution in pre-treatment steps (Daylan et al., 2013)</td>
</tr>
<tr>
<td>Drag-out tank with two stage counter current rinsing steps</td>
<td>Minimization of 88% of rinsing water consumption (Daylan et al., 2013)</td>
</tr>
<tr>
<td>Introduce nitrogen in chromium plating</td>
<td>Minimization of the amount of chromium (Chen et al., 1996)</td>
</tr>
<tr>
<td>Replacing solvent-based degreasing process with aqueous degreasing</td>
<td>Degreasing consumption reduced by 92.9 % (Demirer, 2014)</td>
</tr>
<tr>
<td>Using an evaporative cooler in rinsing system</td>
<td>Reducing the wastewater generation (Munsamy et al., 2014)</td>
</tr>
<tr>
<td>Increase the drainage time to decrease drag-outs</td>
<td>Water consumption reduced by 34.1% (Alkaya and Demirer, 2013)</td>
</tr>
<tr>
<td>Apply counter current rinsing using two rinsing stages</td>
<td>Water consumption reduced by 34.1% (Alkaya and Demirer, 2013)</td>
</tr>
</tbody>
</table>
Table 2. Typical composition of nickel and copper plating baths (Dennis and Such, 1993; ASM Specialty Handbook, 2001)

<table>
<thead>
<tr>
<th>Typical composition of a Watt nickel bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulfate (NiSO₄·6H₂O) 150 to 400 g/L</td>
</tr>
<tr>
<td>Nickel chloride (NiCl₂·6H₂O) or 20 to 80 g/L</td>
</tr>
<tr>
<td>Sodium chloride (NaCl) 10 to 40 g/L</td>
</tr>
<tr>
<td>Boric acid (H₃BO₃) 15 to 50 g/L</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Typical composition of copper plating baths</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cyanide strike bath</strong></td>
</tr>
<tr>
<td>Copper cyanide (CuCN) 22 g/L</td>
</tr>
<tr>
<td>Sodium cyanide (NaCN) 33 g/L</td>
</tr>
<tr>
<td>Sodium carbonate (Na₂CO₃) 15 g/L</td>
</tr>
<tr>
<td><strong>Acid sulfate bath</strong></td>
</tr>
<tr>
<td>Copper sulfate (CuSO₄·5H₂O) 200 to 400 g/L</td>
</tr>
<tr>
<td>Sulfuric acid (H₂SO₄) 45 to 75 g/L</td>
</tr>
<tr>
<td>Additives May be present</td>
</tr>
</tbody>
</table>
Figure 1. Timeline of ion exchange membranes and electrodialysis development (Aly et al., 1989; Baker, 2012; Hoek et al., 2013; Nasef and Ujang, 2012; Sata, 2004; Strathmann, 1992; Tuwiner, 1973; Xu, 2005).
Figure 2. A typical electrodialysis system schematic drawing (Scarazzato et al., 2014).
Figure 3. Literature search process employed in this work.
Figure 4. Number of publications per year since 1990.
Figure 5. Classification of published articles in main themes.
Figure 6. Evolution of number of publications since 1990.
Figure 7. Classification of the 55 articles (samples of the review) for the second topic.
Figure 8. Most evaluated metals reported in the samples of the review for the second main theme.