

COPPER IONS REMOVAL FROM ELECTROPLATING WASTEWATER USING NEW TYPE OF ION EXCHANGE MEMBRANES

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Manuscript received: 30.08.2012; Accepted paper: 07.09.2012;

Published online: 15.09.2012.

Abstract. *In this paper the removal of copper ions from electroplating wastewater has been studied using a three-compartment electro dialysis cell of own construction device (made of PVC) and different type of acrylic ion-exchange membranes containing Purolite A100 or Purolite C150. Several essential parameters for this process (initial copper ions concentration, electrolyte conductivity, pH, massic flow) were taken into account and their influence on the extraction percentage of copper ions was studied for different values of the applied cell current. The electro dialysis cell operates at galvanostatic mode (under constant applied current at electrodes), without the electrolyte recirculation, during one hour. The electrodes used in electro dialysis cell were made of lead 99.9 %. The experimental results show that the extraction percentage of copper ions is over 70%.*

Keywords: *electrodialysis, extraction percentage, acrylic ion exchange membranes.*

1. INTRODUCTION

Copper is a persistent, bio-accumulative and toxic heavy metal that do not decompose in the environment; it is not easily metabolized and can harm human health. Wastewaters from metal finishing, textile industries, electronics industry or washing effluents for remediation of soil contaminated with copper may contain up to 500 mg/L copper, which, depending on the worldwide environmental regulations must be controlled to a permitted level before being discharged into the environment [1].

Electrodialysis is a membrane separation process based on the selective migration of aqueous ions through ion-exchange membrane using an external electric field as the driving force. When an electric current passes through the membrane system, the current is carried by both positive and negative ions in the bulk solution phase, but mainly by the counter ions in the ion exchange membrane due to Donnan exclusion [2 - 4].

Applications of electro dialysis can be commonly found in the environmental and biotechnological industries as well as in the conventional application areas, such as the production of table salt, the industrial effluent treatment and the brackish water desalination. Various investigations have been performed in order to apply electro dialysis technology in

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other fields, including fermentation broth desalination, food processing and metal ion separation, due to its advantages such as being environmentally friendly, economical design, convenience of operation, and low energy consumption [2 - 4].

In this paper the removal of copper ions from electroplating wastewater has been studied using a three-compartment electro dialysis cell and different type of acrylic ion-exchange membranes containing Purolite A100 or Purolite C150. The effects of initial copper ions concentration on the duration of electro dialysis, the effects of solution conductivity, solution pH, massic flow, under the constant applied cell current, on extraction percentage of copper ions was investigated.

2. MATERIALS AND METHODS

The experiments were carried out using electro dialysis cell with three detachable circular compartments, own construction device (made of PVC), with two parallel lead electrodes, separated from each other through two acrylic ion-exchange membranes.

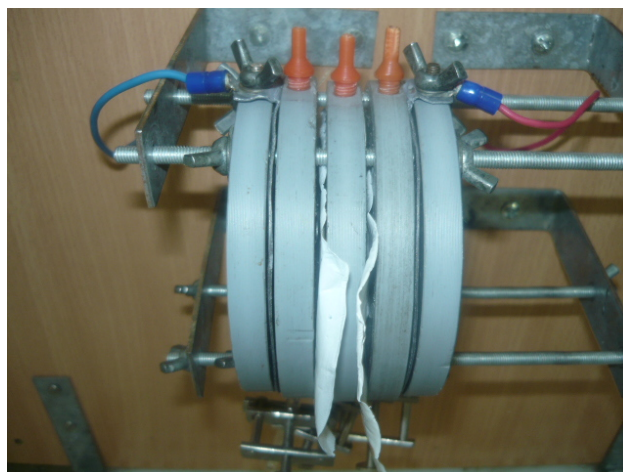


Fig. 1. The experimental electro dialysis cell with three compartments and acrylic ion exchange membranes.

The experiments were conducted by using two different types of bicomponent ion-exchange membranes prepared with ion exchangers (Purolite C150 and Purolite A100) (Purolite Romania). The membranes were prepared from a mixture of 80% acrylic copolymer (90% acrylonitrile : 10% vinyl acetate) and 20 % polyvinyl alcohol with the global concentration of 8% in dimethyl sulfoxide (DMSO), by dissolving the both polymers at 90 °C during 2 h, in the presence of 5% ion exchange resin (A100 or C150), calculated to the polymer mixture.

The polymer solution was cast at room temperature onto a glass plate and a draw-down technique was used to produce films of wet thickness 200 μm . After few seconds, the plate was immersed in a coagulation bath containing 90% isopropanol: 10% water and left there for a half of hour.

The membranes used in this study were prepared at ICECHIM (Polymer Department, Bucharest, Romania). The physical and chemical characteristics of ion exchangers used in the preparation of the membranes are given in Table 1 [5].

Table 1. Typical physical and chemical characteristics of ion exchangers used in the preparation of acrylic ion exchange membranes.

Properties	Purolite A100	Purolite C150
Polymer matrix structure	macroporous styrene-divinylbenzene	macroporous polystyrene crosslinked with divinylbenzene
Physical form and appearance	opaque off-white spheres	opaque spherical beads
Functional groups	tertiary amine	sulphonic acid (R-SO ₃ ⁻)
Ionic form as shipped	FB form	H ⁺
Particle size range	0.3 - 1.2 mm	0.3 - 1.2 mm
Moisture retention	53 - 60%	48 - 53 %
Maxim operating temperature	100°C	130°C
pH range, stability	0 - 14	0 - 14

The electro dialysis cell was separated into three equal volumes by anion- and cation exchange membranes with a working area of 23.32 cm², placed by rubber gaskets in the cell. The rubber gaskets between all body compartments were used to prevent any leakage of the solution. The distance between anode and cathode electrodes was 3.6 cm. The thickness of each compartment with gaskets was 1.28 mm.

A bulk solution containing copper ions was prepared by dissolving copper sulphate (CuSO₄·5H₂O) (Fluka) (Sigma-Aldrich) and sulphuric acid (98%, Merck) (molar ratio 1:1) in distilled water to obtain a concentration of 2 g/L of copper ions.

This synthetic wastewater containing equimolar Cu²⁺ and SO₄²⁻ ions was filled in all compartments of the electro dialysis cell. By applying direct current to the electrodes, Cu²⁺ ions move towards the cathode by passing through a cation exchange membrane. Likewise, SO₄²⁻ ions migrate in the opposite direction by passing through an anion exchange membrane.

In these experiments, at room temperature (25±1°C), the actual working volume was of 29.85 mL/compartment. Electro dialysis was carried out applying a constant anode-cathode current between 0.05 A and 0.1 A (current density 2.144 mA/cm² and 4.288 mA/cm²).

The conductivity of the solutions was measured by a conductivity meter type OK-102/1 (Radelkis, Hungary) that was calibrated using KCl 0.02 N solution. The conductivity meter contains a temperature sensor that allows the automatic compensation with respect to the temperature variation.

The pH of the solutions was measured by a pH meter type HI 8915 (HANNA Instruments, Germany). The pH meter contains also a temperature sensor that allows the automatic compensation with respect to the temperature variation.

The power supply (Protek, Germany) used in the experiments was capable of supplying an applied voltage up to 30 V and a direct current up to 5 A.

The copper ion content from the electroplating wastewater was determined by titration method (Hirschmann Solarus Solar Powered Digital Burette, Germany) using Complexon III 0.01 M and PAN 1% (1 - [Pyridyl-(2)-azo]-naphthol-(2)) as indicator.

Important process parameters including initial copper ions concentration, electrolyte conductivity, solution pH, massic flow and their influence on the extraction percentage of copper ions were examined in the electro dialysis cell for different values of current.

3. RESULTS AND DISCUSSION

3.1. EFFECT OF APPLIED CURRENT

In galvanostatic experiments a constant current is applied to the electro dialysis cell; therefore, the system resistance was obtained from the voltage divided by the current [6]. In this situation the electro dialysis cell can be compared to a group of series resistors, which includes the electrode solution resistance, the electrode reaction resistance, the membrane resistance and the dilute and concentrated solution resistances, respectively [7].

The variation of voltage in time for various values of applied current was recorded.

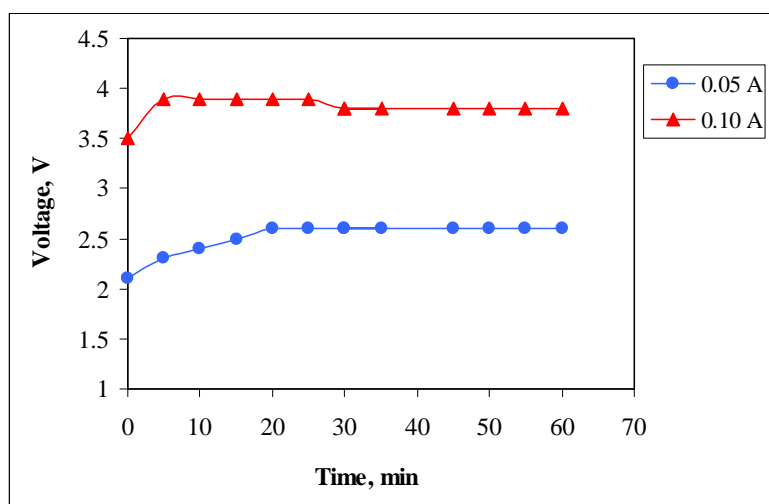


Fig. 2. Variation of cell potential vs. time for different values of current.

Fig. 2 shows that the value of potential increases at the beginning of electro dialysis process and then slightly decreases with time. Lower cell voltage means lower energy consumption. The curves present a maximum value of potential when the stack has passed the initiation stage and its electrical resistance was at a minimum value; then a constant decrease of voltage with increasing of operating time was noticed. As the ion transport during the electro dialysis process produces a dilute solution flowing across the cell, the resistance continuously increases. This resistance increase is only partially compensated by the increasing conductivity of the concentrated solution (anodic compartment). So, the total resistance increases in the electro dialysis cell. This effect, under galvanostatic mode, is observed as the total voltage increase and was attributed to the supply of charged ions to the interface resulting in oxygen evolution reaction [7].

According to literature [6] high current would contribute to more ion transfer in electro dialysis process.

The membrane stack higher potential in electro dialysis system means that higher energy consumption and serious membrane fouling occurred [8].

3.2. EFFECT OF SOLUTION CONDUCTIVITY

The value of solution conductivities measured in the anodic and cathodic compartment were also determined (Table 2).

The conductivity at 0.05 A increases in the anodic compartment and can be attributed to the SO_4^{2-} transport from the central compartment and to the oxygen evolution. At 0.10 A the conductivity in the anodic compartment is lower than for untreated wastewater. In the

cathodic compartment the conductivity decreases for both current values, in comparison with untreated wastewater. This may be attributed to Cu^{2+} transport from the central compartment to cathodic compartment that conducted to copper electrodeposition reaction on the cathode lead [8].

Table 2. The values of conductivity at different values of current.

<i>Time, h</i>	<i>Probes</i>	<i>Conductivity, mS/cm</i>	
		<i>0.05 A</i>	<i>0.10 A</i>
0	untreated wastewater	0.290	0.290
1	treated water from anodic compartment	0.305	0.270
	treated water from cathodic compartment	0.275	0.280

3.3. EFFECT OF SOLUTION pH

Table 3 presents the pH values for the different value of current, measured after one hour, at room temperature.

Table 3. The values of pH at different values of current.

<i>Time, h</i>	<i>Probes</i>	<i>pH</i>	
		<i>0.05 A</i>	<i>0.1 A</i>
0	untreated wastewater	1.35	1.35
1	treated water from anodic compartment	1.28	1.23
	treated water from cathodic compartment	1.26	1.27

The low pH values are due to the acidic electrolyte solutions and can also be attributed to the dissociation of water molecules at the interface of the membrane. Hence, electrical resistance of the solution decreases. It is obvious, that the pH shifting to the stronger acid range, improves the performance of the electro dialysis process [3, 7, 8].

3.4. EFFECT OF MASSIC FLOW

The amount of copper deposited on the lead electrode was estimated in terms of massic flow (J_{massic}) and determined by the following equations:

$$J_{massic} = \frac{\Delta m}{A \cdot t} \quad (1)$$

$$\Delta m = \Delta C \cdot \Delta V \quad (2)$$

$$\Delta C = C_i - C_f \quad (3)$$

where: J_{massic} - massic flow, $\text{g/m}^2\text{h}$; Δm - amount of copper extracted from the solution, g; A - effective working area of the lead electrode, m^2 ; ΔV - initial volume of solution from the cathodic compartment, L; ΔC - variation of the solution concentration, g/L; C_i - initial concentration of electrolyte solution, g/L; C_f - final concentration of the solution after one hour of experiment, g/L.

Table 4. The values of massic flow at different values of current in cathodic compartment.

Current, A	C_o , g/L	C_f , g/L	J_{massic} , g/m ² ·h
0.05	2	0.5952	17.98
0.10	2	0.3392	21.26

From Table 4 one may see that the values of massic flow in the cathodic compartment increase with increasing the values of current because the transported amount of copper ions increased. At low current, the values of the massic flow are small due to the decreased motrice force [11].

3.5. THE EFFICIENCY OF THE ELECTRODIALYSIS CELL

The electro dialysis cell efficiency was evaluated in term of *extraction percentage (EP)* of copper ions [3, 7 - 9, 11 - 13], defined as:

$$EP = \frac{(C_i - C_f)}{C_i} * 100 (\%) \quad (4)$$

where: C_i is the initial concentration of the ion and C_f is the final concentration of the ion at the end of the experiment.

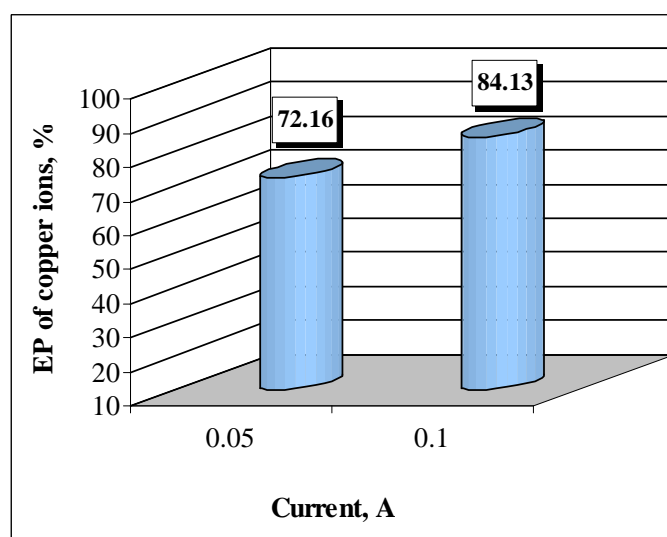


Fig. 3. Extraction percentage of copper ions at different values of current.

Fig. 3 shows that the transport of copper ions increases with increasing value of current and the highest value of extraction percentage of copper ions was obtained at maximum applied current of 0.10 A (current density of 4.288 mA/cm²) [11 - 13]. The formation of copper ions increases at higher value of current and low pH.

CONCLUSIONS

As a result of the investigations on the proposed electro dialysis cell tested for the removal of copper ions from an electroplating wastewater, under the constant current conditions, one may deduce the following conclusions:

- the potential value increases in the beginning of electro dialysis process and then decreases in time. The curves present a maximum value of potential when the stack has passed the initiation stage and its electrical resistance was at a minimum; then constant decrease of voltage with increasing the operating time was observed. Lower cell voltage means lower energy consumption;

- under galvanostatic mode, it is observed the total voltage increasing and this was attributed to the supply of charged ions to the interface resulting in oxygen evolution reaction;

- high current would contribute to more ion transfer in electro dialysis process;

- the electrical conductivity increases in the anodic compartment (at 0.05 A) in comparison with the untreated solution and this can be attributed to the SO_4^{2-} transport from the central compartment and to the oxygen evolution. The conductivity decreases in the cathodic compartment for both current values in comparison with the untreated solution and this can be attributed to Cu^{2+} transport from the central compartment to cathodic compartment, that conducted to copper electrodeposition reaction on the cathode lead;

- due to the acidic character of the electrolyte solutions, the low pH values can be attributed to the dissociation of water molecules at the interface of the membrane;

- the values of massic flow in the cathodic compartment increase with increasing the values of current because the transported amount of copper ions increased. At low current the values of the massic flow are small due to the decreased motrice force;

- the transport of copper ions increase with increasing value of current and the highest value of extraction percentage of copper ions (more than 84%) was obtained at maximum applied current of 0.10 A.

Acknowledgements: Simona Căprărescu acknowledges the financial support of strategic grant Grant CNCSIS, TD CH410806, code 26, cofinanced by The National Authority for Scientific Research (CNCSIS, Romania). Violeta Purcar acknowledges the financial support of strategic grant POSDRU/89/ 1.5/S/58852, Project „Postdoctoral programme for training scientific researchers“ cofinanced by the European Social Found within the Sectorial Operational Program Human Resources Development 2007-2013“. Special thanks go to the following people for their logistic support: Mrs. Mariana Andrei and Mr. Corneliu Andrei from University Politehnica of Bucharest.

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