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A 3-cell electrodialysis system for the removal of copper ions from electroplating wastewater

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In this paper, the removal of ionic copper from a electroplating waste streams has been studied using a three-compartment electrodialysis cell and different type of ion-exchange membranes. A series of essential parameters for this process were taken into account (electrolyte concentration, conductivity, *p*H) and their influence on the percent extraction was studies for different values of the applied cell voltage. Chemical stability of ion exchange membranes was investigated by Fourier transformed infrared spectroscopy. The experimental results show that the percent extraction of copper ions is higher by using electrodialysis, in this case were obtained values above 80% for concentration of copper ions of 8000 ppm.

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1. Introduction

The removal of heavy metals from industrial wastewater can be successfully carried out by the ion-exchange membrane assisted electrodialysis process, which is a combination of ion exchange with electrodialysis.

The properties of ion-exchange membranes are determined by different parameters, such as the density of the polymer network, the hydrophobic or hydrophilic character of the matrix polymer and the type and concentration of the fixed charges in the polymer, and the morphology of the membrane itself. The most important properties of ion-exchange membranes are: high degree of selectivity for ions given charge, low electrical resistance, physical strength, resistance to deterioration at high temperatures, good mechanical and form stability, high chemical and thermal stability and low production costs [1-4].

Electrodialysis is an electrochemical process for the separation of ions. They pass through ion exchange membranes from one solution to another under the influence of an electrical potential difference used as a driving force. In a typical electrodialysis cell, a series of anion- and cation exchange membranes are alternately arranged in a filter press-like system between two chemically and electrochemically inactive electrodes, positioned at the end of the stack, so that a diluted flow and concentrated flow are the results of the separation processes taking place. When a d.c. potential gradient is applied between two electrodes, positively charged cations move toward the cathode, pass through the negatively charged cation-exchange membranes and are retained by the positively charged anion-exchange membrane. On the other hand, negatively charged anions move toward the anode, pass through the positively charged anion exchange membranes and are retained by the negatively charged cation-exchange membranes. At the end, ion concentration increases in alternate compartments with simultaneous ion depletion in other compartments [3-5].

Electrodialysis has found industrial uses in such diverse applications as brackish water desalination, recovery of metals and salts from industrial wastewater, acid recovery, wastewater treatment and heavy metal recovery from plating rinse water [6].

Electrodialysis is being used successfully on rinses from such types of electroplating baths as gold, platinum, silver, copper, nickel, tin, palladium, cadmium, tin-lead and zinc [6].

In this paper the effect of different operating conditions for the separation of copper ions from a galvanic coating plant wastewater by an experimental electrodialysis cell was studied.

The electrodialysis performance was evaluated in term of *percent extraction* [3, 7-10]. It is calculated using following equation:

$$percent\ \ extraction = \frac{\left(C_0 - C_f\right)}{C_0} \cdot 100 \qquad (1)$$

where C_0 is the initial ion concentration and C_f is the ion concentration at the end of the experiment.

2. Experimental part

The experiments were carried out in an electrodialysis cell, made of Polyamide 6 reinforced with glass fibre, separated from each other through two ion-exchange membranes (see Fig. 1).

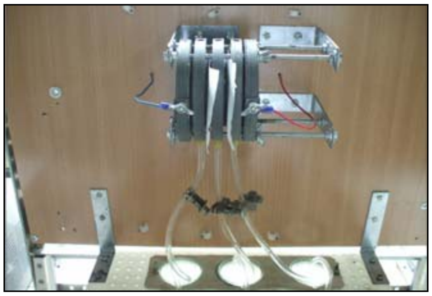

Fig. 1. The experimental electrodialysis cell with three compartments

In these experiments are used different types of ion-exchange membranes prepared with acrylic component (melana, 10%) (Melana International Pte Ltd), solvent dimethylformamide (Sigma-Aldrich) and ion exchangers (Purolite A400 and Purolite C104) (Purolite Deutschland GmbH, Germany)**.** The membranes used in this study were prepared by ICECHIM (Polymer Department, Bucharest, ROMANIA). The characteristics of ion exchangers used in the preparation of membranes are listed in Table 1 [10, 11].

Table 1. Characteristics of ion-exchange membranes used in electrodialysis.

Properties	**Purolite A400**	**Purolite C104**
Polymer Matrix Structure	Gel polystyrene cross-linked with divinylbenzene	Gel polyacrylic crosslinked with divinylbenzene
Functional groups	Type I Quaternary Ammonium	Carboxylic acid
Appearance	Spherical beads	Spherical beads
Ionic form as shipped	Cl^-	H^+
Moisture holding capacity, %	48-54	45-55
Operating Temperature	100ºC	120ºC
*p*H limits	0-14	0-14

In electrodialysis cell stack the anion-exchange membrane was placed next to the anode and the cation-exchange membrane was placed next to the cathode. The electrodes were made of lead 99.9%. This metal was preferred because is chemically and electrochemically inactive with respect to the solution ions and electrode processes taking place.

The distance between anode-cathode electrodes was 52 mm. The effective area of each membrane and electrode was of 28.26 cm^2.

In these experiments, the actual working volume which was subjected to the electrodialysis process at room temperature (25°C), for 3 h, was of 48.04 ml/compartment. Electrodialysis was carried out applying a constant anode-cathode voltage between 3.5 and 9 V, applied for replicated experiments saved for the voltage.

Synthetic wastewater solutions, reassembling the wastewater from copper electroplating waste streams were prepared by dissolving copper sulphate ($CuSO_4 \cdot 5H_2O$) and sulphuric acid (Merck, 98%) in deionised water to obtain concentrations between 2000 ppm and 8000 ppm of copper ions [10, 12-16]. The molar ratio between the cooper sulphate and sulphuric acid was kept to 1:1.

The solution is pumped into the electrodialysis unit and one has the option to operate it either as a batch/stagnant system or as a continuous system, at a controlled flow rate.

The effects of applied potential and initial concentration on the percent extraction were examined in the electrodialysis cell. One has also recorded the variations in ionic conductivity and *p*H in the cell compartments.

The conductivity of the solutions was measured by a conductivity meter type WA-100 ATC (Voltcraft, Germany) that was calibrated using KCl 0.02 N solution. The solutions *p*H measured using a *p*H meter type HI 8915 (HANNA Instruments, Germany). The *p*H 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 delivering an applied voltage up to 30 V and a total current up to 20 A.

The chemical structure of the membranes was confirmed by an attenuated total reflection Fourier transform infrared spectroscopy (FT-IR, Tensor 37 Bruker). A spectrum, collected as the average of 64 scans with a resolution of 4 cm^{-1}, was recorded from 4000 to 400 cm^{-1} for the ATR mode using the Golden Gate unites.

3. Results and discussions

The variation of cell current as function of time was recorded for various copper ions concentrations and various values of applied voltage (see Figs. 2 and 3).

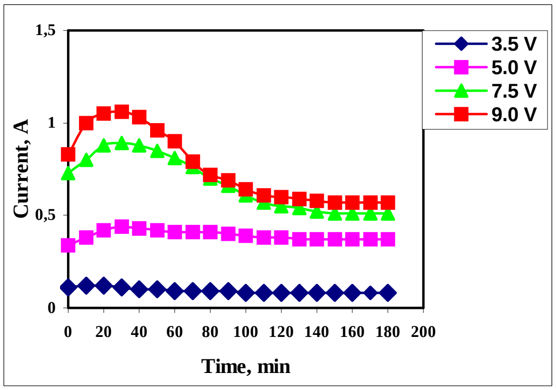

Fig. 2. Variation of cell current as function of time for different values of applied voltage and value of the copper ion concentration of 2000 ppm

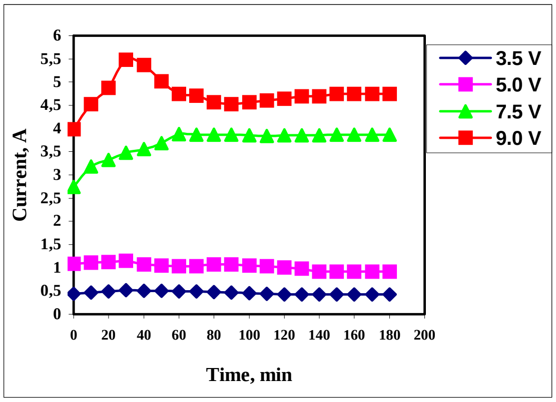

Fig. 3. Variation of cell current as function of time for different values of applied voltage and value of the copper ion concentration of 8000 ppm

Figs. 2 and 3 shows that the current value increases with increasing electrodialysis time, because the overall stack electrical resistance decreases. This fact is due to the ion transfer processes. The curves present a maximum current value when the stack has passed the initiation stage and its electrical resistance was at a minimum and then decreases with increasing of operating time. After an induction period (40 min.), the overall conductivity of the cell decreased. This fact is due to the decrease of the extracted copper ions ions concentrations. After 100 minutes the current value is constant, this implies that the copper ions could still penetrate the cation-exchange membrane even under saturation conditions. The current value increases with increasing ionic concentration, being explained by the high ionic conductivity. The highest value of current being obtained for the highest value of applied voltage of 9 V. Similar results were reported also in recent publications [4, 6, 10].

In Table 2 and Table 3 are showed the values of conductivities for various solutions, measured at 25 ^{o}C, for various applied voltages. The values of conductivities for various solutions increase in the anodic compartment with increasing applied voltage. This fact is due to the oxygen evolution, the remaining excess protons will increase the overall proton concentrations increasing the value of conductivity in this compartment. In the cathodic compartment decrease of conductivity with increasing applied voltage is a direct consequence of the electrodeposition reaction of copper on the cathode, decreasing the copper ions conductivity contribution. This fact is confirmed by the metallic copper layer deposited onto the lead cathode that can be visually noticed at the end of the experiment when the cell is disassembled (see Figs. 4 and 5).

Table 2. The values of conductivity of the different values of applied voltage at 2000 ppm.

Time, h	**Probes**	**Conductivity, mS/cm**			
		2000ppm			
		3.5 V	5.0 V	7.5 V	9.0 V
0	untreated wastewater	30	30	30	30
3	treated water from anodic compartment	42	50	69	73
	treated water from cathodic compartment	34	23	11	9

Table 3. The values of conductivity of the different values of applied voltage at 8000 ppm.

Time, h	**Probes**	**Conductivity, mS/cm**			
		8000ppm			
		3.5 V	5.0 V	7.5 V	9.0 V
0	untreated wastewater	105	105	105	105
3	treated water from anodic compartment	141	168	221	360
	treated water from cathodic compartment	120	95	68	50

Figs. 4 and 5 shows that copper deposits on the lead electrode are not compact. These deposits can be used to obtain the copper wires, copper cylinders. Microscopic image of copper deposited at lead cathode was obtained by using a digital microscope (Intel QX3, Germany) (Fig. 5).

Fig. 4. The metallic copper layer deposited onto the cathode.

Fig. 5. Microscopic image 60 X of copper deposited onto the Pb electrode.

Tables 4 and 5 present the *p*H values for the different concentration of solutions at different applied voltages, measured after 3 h, at room temperature. Low *p*H values are due to the acidic electrolyte solutions.

Table 4. pH values at various values of applied voltage at 2000 ppm.

Time, h	**Probes**	***p*H**			
		2000 ppm			
		3.5 V	5.0 V	7.5 V	9.0 V
0	untreated wastewater	2.00	2.00	2.00	2.00
3	treated water from anodic compartment	2.03	2.24	2.23	2.51
	treated water from cathodic compartment	2.28	2.31	2.49	2.39

Table 5. pH values at various values of applied voltage at 8000 ppm.

Time, h	**Probes**	***p*H**			
		8000 ppm			
		3.5 V	5.0 V	7.5 V	9.0 V
0	untreated wastewater	1.94	1.94	1.94	1.94
3	treated water from anodic compartment	2.44	1.58	2.47	2.05
	treated water from cathodic compartment	1.67	2.19	1.91	2.34

The value of the percent extraction parameter was calculated using relation (1) in accordance with the established procedure [4-7] in order to evaluate the performance of the electrodialysis process.

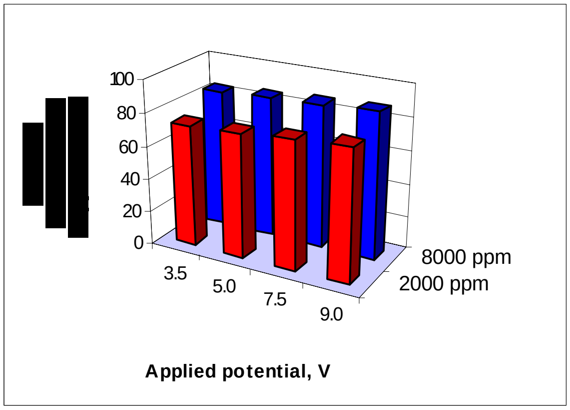

Fig. 6. Percent extraction of copper ions after 3 h of treatment for different values of applied voltage at 2000 ppm and 8000 ppm, respectively.

Fig. 6 shows that the percent extraction of copper ions increases with increasing initial concentration solutions and applied cell voltage. The percent extraction of copper ions is greater at higher concentration of copper ions and higher applied voltage (8000 ppm and 9 V) because the phenomenon of concentration polarization is more important at higher concentrations.

The chemical structure of blank membranes and membranes used at various copper ions concentrations and at different values of applied cell voltage (anion- and cation-exchange membranes, respectively) was investigated by the FT-IR spectroscopy (see Figs. 7-10). The samples were examined before and after exposure to electrodialysis process.

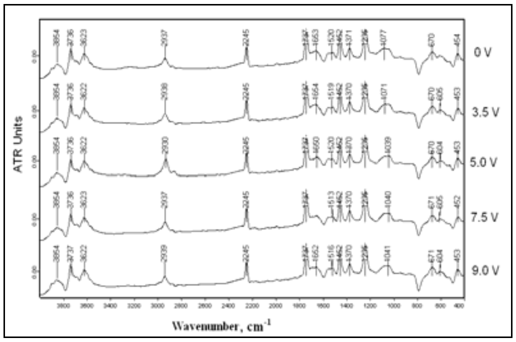

Fig. 7. FT-IR spectra of anion-exchange membranes using different values of applied potential, at 2000 ppm.

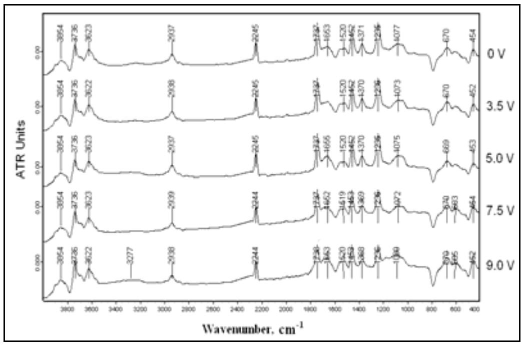

Fig. 8. FT-IR spectra of anion-exchange membranes using different values of applied potential, at 8000 ppm.

After evaluation of FT-IR spectra of anion-exchange membranes (Figs. 7 and 8), were not observed significant modification between the samples, indicating that membranes were not damaged during the electrodialysis. Appearance of a peak in the range 2937-2939 cm^{-1} for anion exchange, may be assigned to –CH$_2$- (acrylic) (stretching vibration, asymmetric C-H) (crosslinked polystyrene). The peak at 2244 cm^{-1} can be assigned to -C≡N bond (stretching vibration) [17, 18].

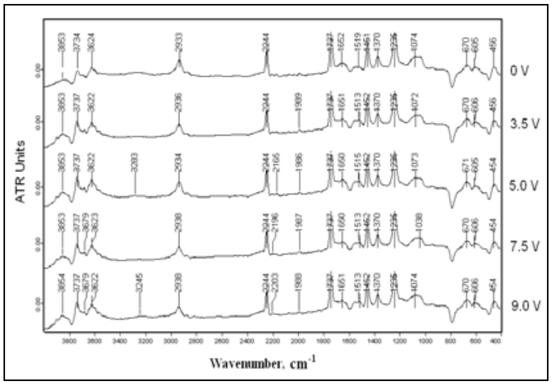

Fig. 9. FT-IR spectra of cation-exchange membranes using different values of applied potential, at 2000 ppm.

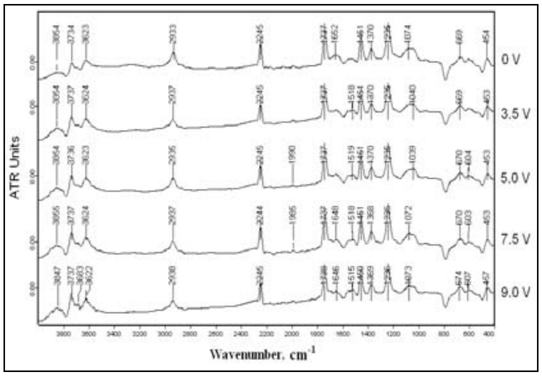

Fig. 10. FT-IR spectra of cation-exchange membranes using different values of applied potential, at 8000 ppm.

From Figs. 9 and 10 was observed a medium intensity band at 1737cm^{-1} which may be due to C = O bond (stretching vibration), the resulting non-ionic carboxyl groups (-COOH, -COOCH$_3$), and can be attributed to carboxylic acids or esters. Asymmetric and symmetric stretching vibration of the ionic carboxylic groups (-COO$^-$) appears at ~1651 cm^{-1} for all cation- exchange membrane.

A medium intensity band is observed in all spectra at 1235 cm^{-1} and is due to R-CH$_3$ group (deformation vibration of the C-H link).

In case of applied potential (9 V) for all cation-exchange membranes, the shifted to higher wave numbers was observed at 2938 cm^{-1} compared with the blank membranes (0 V) where the peak appears at 2933 cm^{-1}. This fact can be due to C-H linkage (stretching vibration) which occurs during the electrodialysis process. Another shift was observed at the corresponding wave number of ~453 cm^{-1}, which increase with increasing concentration. This peak can be assigned to stretching vibration of C-C linkage (fig. 9 and 10) [17, 18].

4. Conclusions

Based on the work presented here we conclude the following in regards to electrodialysis associated with the ion exchange membranes for the removal of copper ions from electroplating wastewater at different operating conditions:

- the value of the current increases with increasing initial concentration of copper ions and applied voltage, the highest current being obtained for an applied voltage of 9 V;
- the percent extraction of copper ions increases with increasing applied voltage reaching values above 80% for concentration of copper ions of 8000 ppm;
- anion exchange membrane in conjunction with electrodialysis process, has the potential to be used as an efficient aid for the removal and recovery of Cu^{2+} from wastewaters.

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