

REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTIONS USING CATION- AND ANION-EXCHANGE MEMBRANES BY ELECTRODIALYSIS PROCESS

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În lucrarea de față a fost investigată variația randamentului de extracție a ionilor de Cu^{2+} în funcție de concentrația inițială a soluției și de tensiunea de lucru aplicată celulei de electrodializă, pentru un sistem de lucru având drept componentă principală o celulă de electrodializă cu trei compartimente, utilizând membrane schimbatoare de ioni de tipul Purolite C104 și Purolite A400.

In this paper one has investigated the dependence of the removal efficiency for Cu^{2+} ions on the initial concentration and applied working voltage for an electrodialysis system consisting of a three-compartment cell using ion-exchange membranes such as Purolite C104 and Purolite A400.

Keywords: electrodialysis, ion-exchange membranes, copper, electrochemical process, synthetic wastewater

1. Introduction

Electrochemical technology has contributed successfully to the removal of heavy metals from industrial process waters. The usefulness of the various electrochemical techniques depends on the nature of the metal to be removed and the composition of the liquid to be purified [1].

Electrodialysis is an electrochemical separation process where under the influence of an applied electrical field and with the help of semi-permeable membranes ionic species from an aqueous solution are diverted through the

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membrane obtaining two or more effluent streams, one depleted in ionic species and the other enriched in the very same ionic species. Taking into account the versatility of this process, electrodialysis is a promising technique for the treatment of effluents to recover valuable substances for further re-use or to treat polluted effluents [2, 6]. Electrodialysis is applied nowadays as a recovery method for a large number of metals (Au, Pt, Ni, Cu, Ag, Pd, Cd, Zn, Sn, Pb) from plating baths [5, 11].

A category of heavily used membranes in electrodialysis is that of the ion-exchange membranes. These are placed alternately, (i.e. a cation-exchange membrane and an anion-exchange membrane and so on between an anode and a cathode), constituting an electrodialysis stack reactor [2, 7].

For efficient economic operation, the membranes have the following properties:

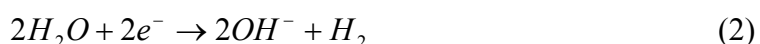
- high degree of selectivity for ions of given charge;
- low electrical resistance, with high water content and high concentration of fixed charges;
- low degree of water transport (electroosmosis reduces efficiency of the whole process and must be avoided);
- inertness with no deterioration the presence of chemical and biological material;
- physical strength;
- resistance to deterioration at high temperatures [3].

Electrodialysis with ion-exchange membranes represents one of the most important membrane methods of treatment of industrial effluents discharged [9].

In this work we are proposing an electrodialysis cell stack consisted of a three compartment cell, separated from each other by two ion-exchange membranes. Upon application of a potential, the ions diffuse through respective ion exchange membranes akin to the electrodialysis cell. However, the cations that diffuse through the cation exchange membrane may be reduced to metal at cathode:



Depending upon the applied potential, hydrogen evolution reaction may also take place at cathode, being a competitive reaction:



In this particular case the anions of SO_4^{-2} diffuse through the anion exchange membrane and reach the anode. At the anode, oxygen evolution reaction takes place:



An important parameter used to evaluate the efficiency of the electrodialysis process is the removal efficiency, also called *percent extraction*, defined as [4]:

$$\text{percent extraction} = \frac{(c_0 - c_f)}{c_0} 100 \quad (4)$$

where c_0 is the initial ion concentration and c_f is the ion concentration at the end of the experiment.

2. Experimental

2.1. Materials

The membranes used for this work were anion-exchange membrane (Purolite A400) and cation-exchange membrane (Purolite C104); copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sulphuric acid and deionised water were used to prepare the solutions. The electrodes were made of lead 99.9%, in order to allow an easy construction and integrability inside the cell. The lead is the insoluble electrode (it does not release cations in solutions) and allows the discharge of O_2 .

2.2. Experimental procedure

The electrodialysis cell stack consisted of a three compartment cell, separated from each other by two ion-exchange membranes. The lead electrode anode was placed next to the anion-exchange membrane and the lead cathode was placed next to the cation-exchange membrane. The membranes and the electrodes surface area was of 28.26 cm^2 .

The heavy metal contaminated solution is pumped into the electrodialysis unit, each stack being separated by a spacer, allowing the solution either to be stagnant or to flow at a controlled flow rate depending on the chosen operating conditions. Under the influence of the applied electrical potential across the stack membranes the cations in solution migrate toward the cathode, and anions toward the anode. When a cation encounters a semi-permeable cation membrane, it passes through. Similarly, anions migrate toward the anode, pass through a semi-permeable anion membranes. In the case of ion-exchange membranes, the process is somehow similar, the only difference being that the main process of passing through the membranes is replaced with that of an ionic exchange (cationic or anionic depending on the membrane type) process.

Synthetic wastewater reassembling the wastewater from copper electroplating was prepared by dissolving copper sulphate and sulphuric acid in

deionised water to obtain concentrations of 500 ppm, 1000 ppm, 2000 ppm and 4000 ppm. The ratio between the copper sulphate and sulphuric acid was 1:1.

The conductivity of the solutions was measured by a conductivity meter WA-100 ATC (Votcraft, Germany) 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.

3. Results and Discussions

In these experiments the actual working volume which was subjected to the electrodialysis process at room temperature (25°C) for 3.5 h under potentiostatic conditions (a constant anode-cathode applied voltage of 6.5 V) was of 48.04 ml/compartiment. One has chosen the value of 6.5 V, in accordance with recent reports by Roni F. Dalla Costa et al. [4] and Abo-Ghander N. S. et al. [6], as this will compensate best the ohmic drop in electrolyte solutions for the anode-cathode distance of 50 mm. The variation of current in time for the applied voltage was recordered for various initial concentrations of copper ions.

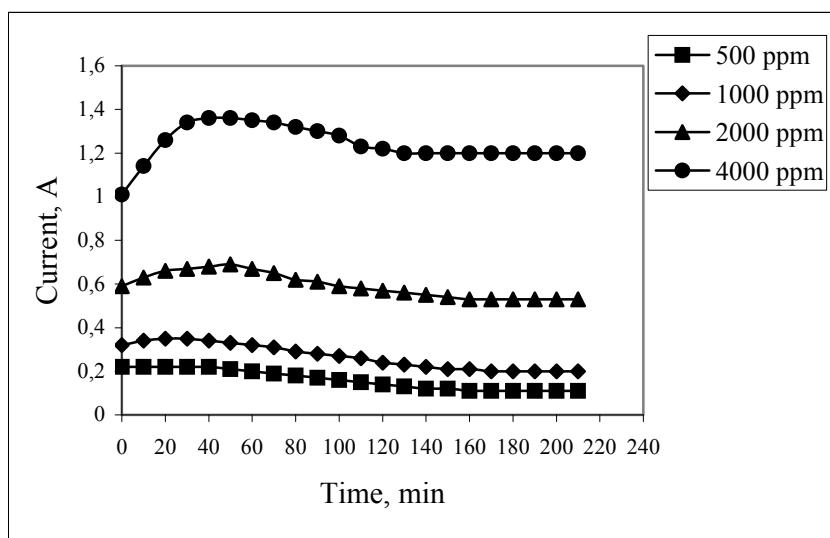


Fig. 1. Variation of cell current in time for different concentrated solutions

Fig. 1 shows that the current initially increases with increasing time because the stack resistance gradually decreased due to ion transfer and decreased after showing a maximum value when the stack resistance was the minimum value. These results are also in agreement with recent reports by Keun Ho Choi et al. [5].

Structural change of anion- and cation-exchange membrane under the influence of the applied constant voltage was investigated by the FTIR spectra between the virgin membrane and that used at different wastewater concentrations (see fig. 2 and fig. 3).

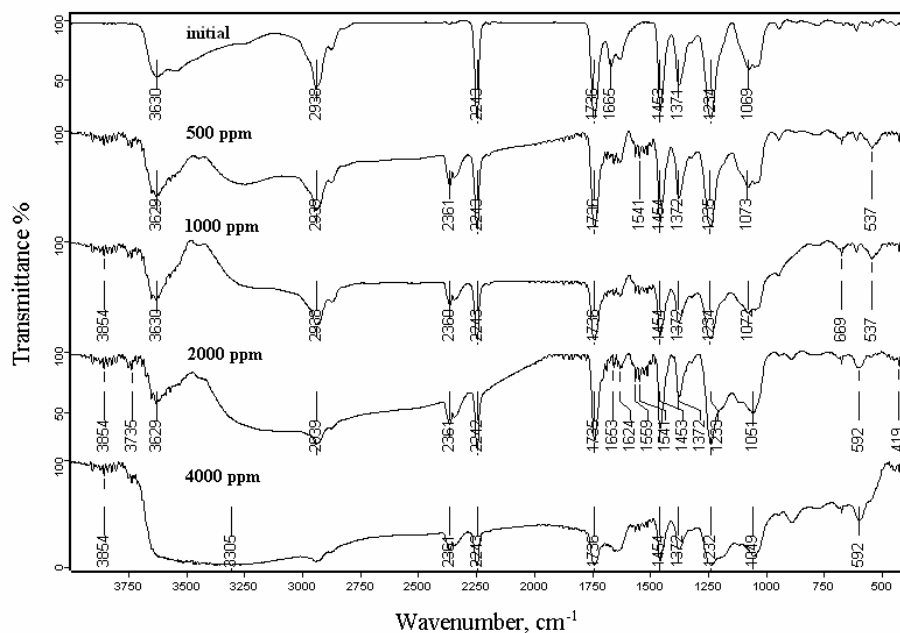


Fig. 2. FT-IR spectra of anion-exchange membranes using different concentrated solutions

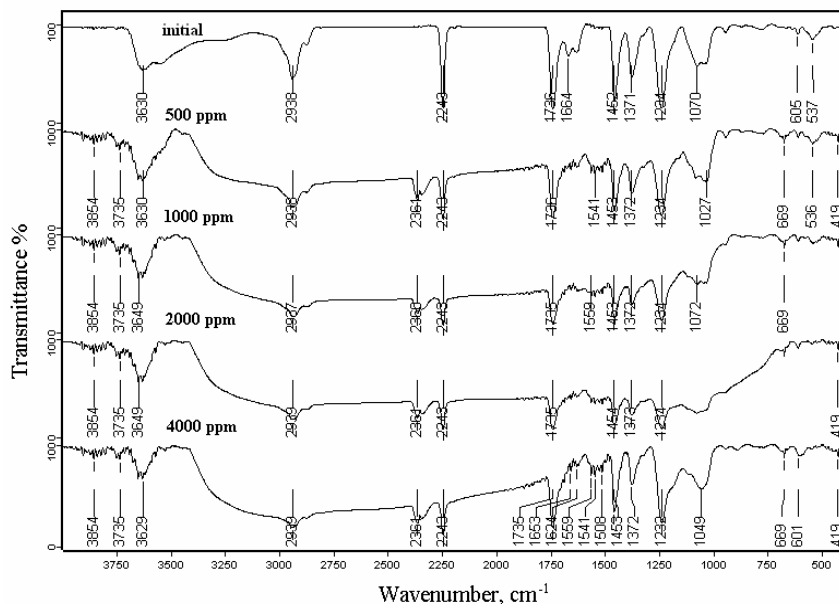


Fig. 3. FT-IR spectra of cation-exchange membranes using different concentrated solutions

Fig. 2 and fig. 3 show that the tertiary amine groups are formed from the quaternary ammonium groups on the anion-exchange membrane surface where ion depletion occurs under the influence of the applied constant voltage. The occurrence of increased water dissociation is considered to be caused by the protonation and deprotonation of the tertiary amine groups in the anion-exchange membrane. For these samples, the tertiary amine groups give a strong absorption band in the spectral region at $\sim 3630\text{ cm}^{-1}$ and 2938 cm^{-1} respective.

The wastewater conductivity of solutions from anodic and cathodic compartment was also measured. In Tabel 1 one may see that, as expected, the values of conductivities for various solutions increase in the anodic compartment. This is due to the fact that following the oxygen evolution the leftover protons, in the presence of the sulphate ions, regenerate the sulphuric acid, increasing the value of conductivity in this compartment. The apparently anormal decrease of conductivity in the cathodic compartment is a direct consequence of the electrodeposition reaction of copper on the cathode, decreasing the copper ions conductivity and consequently the value of the respective conductivity. This is confirmed by the metallic copper layer deposited onto the cathode that can be visually noticed at the end of the experiment when the cell is disassembled and also by gravimetric evaluation (see tabel 2).

Tabel 1

The values conductivity of the different solutions

Probes	Conductivity, mS			
	500 ppm	1000 ppm	2000 ppm	4000 ppm
untreated wastewater	11,0	21,0	34,0	63,0
treated water from anodic compartment	25,7	37,0	67,0	135,0
treated water from cathodic compartment	3,0	5,0	15,0	34,0

Tabel 2

The gravimetric evaluation for different solutions

Concentration, ppm	Electrodeposited mass of copper, g
500	0,0615
1000	0,1231
2000	0,2479
4000	0,4392

The value of the percent extraction parameter was calculated using relation (4) in order to evaluate the efficiency of the electrodialysis process.

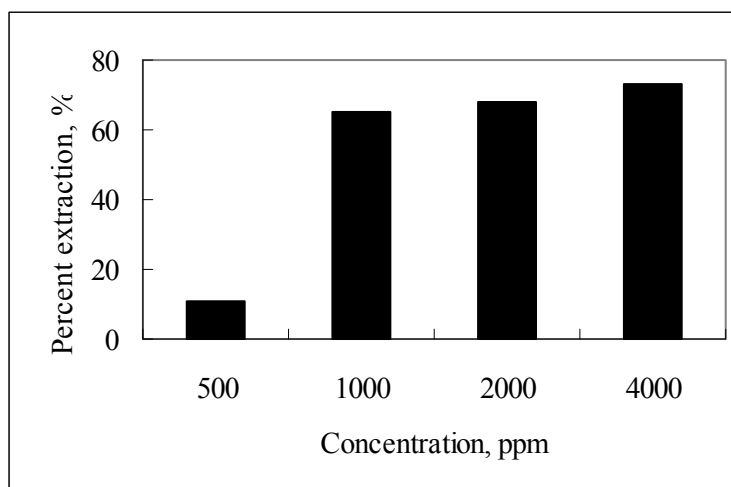


Fig. 4. Percent extraction of copper ions after 3,5 h of treatment for different concentrated solutions

Fig. 4 shows that the percent extraction increased with increased initial concentration solutions. The increase is very sharp from concentrations of 500 ppm to that of 1000 ppm and only marginally after 1000 ppm suggesting that this process may be applied with increased efficiency starting from 1000 ppm upwards, below this limit the cell acting mainly as an electrolysis cell rather than an electrodialysis cell.

These results are also in agreement with recent reports by Roni F. Dalla Costa et al. [4] that proves the percent extraction of copper ions is higher by using electrodialysis.

4. Conclusions

As a result of the investigations of the above electrodialysis associated with the wastewater treatment from electroplating industry one may deduct the following conclusions:

- the FT-IR study revealed that the tertiary amine groups are formed from the quaternary ammonium groups on the anion-exchange membrane surface where ion depletion occurs under the influence of the applied constant voltage;
- the occurrence of increased water dissociation is considered to be caused by the protonation and deprotonation of the tertiary amine groups in the anion-exchange membrane;
- as far as the applicability of this process is concerned, the lower applicable wastewater concentration limit seems to be around 1000 ppm, below this limit the cell acting mainly as an electrolysis cell (90%) and only partially as an electrodialysis cell (10%), below 500 ppm being recommended the use of semipermeable membranes instead of the ion exchange membranes.

REFERENCES

- [1] *L. J. Janssen and L. Koene*, Chem. Eng. J., **vol. 85**, 137, 2002
- [2] *Juliette Lambert, Mohammed Rakib, Gérard Durand, Mario Avila-Rodríguez*, Treatment of solutions containing trivalent chromium by electrodialysis, Desalination, **vol. 191**, 2006, pp. 100–110
- [3] *D. I. Vaireanu*, Electrochemistry and corrosion, AGIR Publishing House, Bucuresti, 2006, pp. 102-104
- [4] *Roni F. Dalla Costa, Claudia W. Klein, Andrea M. Bernardes and Jane Zoppas Ferreira*, Evaluation of the Electrodialysis Process for the Treatment of Metal Finishing Wastewater, J. Braz. Chem. Soc., **vol. 13**, no. 4, 2002
- [5] *Keun Ho Choi and Tae Young*, Removal of zinc ions in wastewater by electrodialysis, Korean J. Chem. Eng., **vol. 19**, no. 1, 2002, pp. 107-113
- [6] *N. S. Abo-Ghander, S. U. Rahman, S. M. J. Zaidi*, A modified electrodialytic cell to recover heavy metals from wastewater, Portugaliae Electrochimica Acta, **vol. 24**, 2006, pp. 367-376
- [7] *T. Sata, T. Sata and W. Yang*, Studies on cation-exchange membranes having permselectivity between cations in electrodialysis, J. Membr. Sci., **vol. 206**, 2002 pp. 31-60
- [8] *S. Koter, A. Warszawski*, Electromembrane Processes in Environment Protection, Polish Journal of Environmental Studies, **vol. 9**, no. 1, 2000, pp. 45-56
- [9] *V. E. Santarosa, F. Peretti, V. Caldart, J. Zappas, M. Zeni*, Study of ion-selective membranes from electrodialysis removal of industrial effluent metals II: Zn and Ni, Desalination, **vol. 149**, 2002, pp. 389-391
- [10] *D. I. Vaireanu*, Depoluarea electrochimică a apelor reziduale, Ed. Printech, Bucuresti, 2000, pp. 33-39
- [11] *D. I. Vaireanu*, Metode electrochimice aplicate în protecția mediului, Ed. Printech, Bucuresti, 2007, pp. 35-37