

THE USE OF ELECTRODIALYSIS FOR Cu^{2+} REMOVAL FROM WASTEWATER

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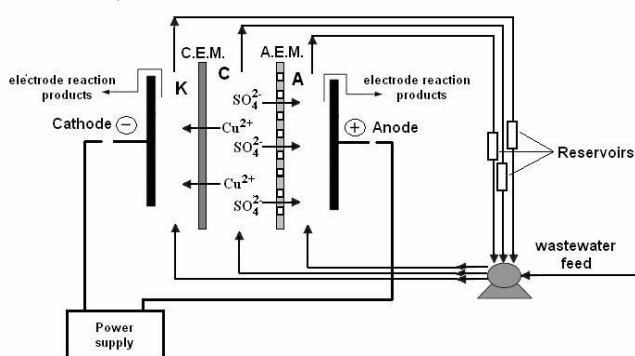
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A study of the Cu^{2+} removal from synthetic wastewater solutions, using different polymer ion exchanging membranes based on the copolymer acrylonitrile-vinyl acetate- α methyl styrene and containing small quantities of anion (Purolite A500) or cation exchange resins (Puropack PPC100) is presented. A three circular compartments electro dialysis cell was used. This electro dialysis unit worked under a constant applied voltage (9 V), in batch mode, with the electrolyte recirculation.

The effect of initial copper ions concentration and flow rate on the duration of electro dialysis removal of copper ions was evaluated. The conductivity value, pH value and temperature of solution were measured at the end of electro dialysis. The percent extraction (PE) of copper ions and energy consumption were determined. The results demonstrated that the ion removal rates from the synthetic solution increased with solution flow rate and the PE of copper ions increased over 88%, when initial copper ions concentration was high (4 g/L). The optimal flow rate and energy consumption values to remove copper ions are reported.



INTRODUCTION

The removal and recovery of toxic and polluting metal ions from industrial wastewaters produced by metal plating, metal finishing, mining, automotive, aerospace and battery is an important challenge to avoid the major causes of water and soil pollution. These metals have negative impact on the ecosystem and also have large economic and public-health significance.¹⁻⁴

Different methods have been detailed and applied for the removal and recovery of toxic heavy metal ions from sea water and industrial wastewaters some of which include using of ion exchange resins and chelating resins, liquid extraction, electro dialysis, chemical precipitation, membrane filtration, biosorption.¹⁻⁵

Electro dialysis is an electrochemical process for separation of ions across charged membranes by passing them from one solution to another under the influence of an electrical potential difference

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used as a driving force. The basic principles and many applications of electro dialysis were reviewed in the literature.¹⁻¹⁶

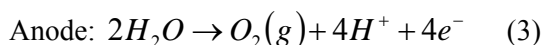
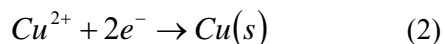
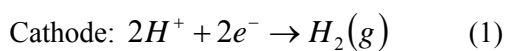
In the literature, it was shown that the geometry of electro dialysis cells namely the compartments with diluted and concentrated solutions is identical and that the linear flow velocities in compartments should be equal and in the same direction for avoid hydrostatic pressure differences.⁶

In this paper, the effect of initial copper ions concentration and flow rate was examined in an own-constructed electro dialysis cell for three values of copper ion concentration. The value of conductivity, of *pH* and of temperature of the solution was measured before and after electro dialysis processes. The laboratory electro dialysis cell efficiency was evaluated in term of *percent extraction* (PE).

RESULTS AND DISCUSSION

Effect of flow rate on electro dialysis process

In acid medium the following reactions occur at the lead electrodes during the operation of the electro dialyser:^{5,7,8,13}



The formation and evolvment of H_2 and O_2 gases that occur at the cathode electrode and anode electrode respectively reduce the process efficiency and increase the resistance of the electro dialysis cell. Due to this fact, a small hole was made at top of the electro dialysis system to release gases on the plate of the electro dialysis cell.

The values of *pH*, conductivity and temperature of solution were measured before (feed wastewater) and after 3 h of treatment.

Table 1 shows the values of *pH* and conductivity of solution at various concentration of Cu^{2+} in feed solutions and at two values of flow rate. It was observed that the *pH* values are low for all solutions, because the electrolyte solutions have acid character. Higher *pH* values were obtained for cathode compartment. The explanation of this *pH* increase could be that, at low *pH*, the high H^+ concentrations compete with Cu^{2+} at the cathode surface. These results given in this study are similar with those obtained in our previous work.²

The value of *pH* of feed solution was not very different in comparison with that of treated

solutions in all compartments. Because, during the experiments we observed that the *pH* of the treated solutions from all compartment does not strongly affect the percent extraction of Cu^{2+} it was no need to adjust the *pH* and hence to add any chemical before and after treatment.

The electrical conductivity differences between the anode, central and cathode compartments (Table 1) indicated that the ion exchange membranes used in the electro dialysis system have performed ion exchange, especially at high ion concentrations. In the continuous electro dialysis process the transport of ions through ion exchange membrane produces a dilution of solution flowing across the cell and the resistance continuously decreases. The dilution of the solution means that ion was removed from solution. If the ion was removed from solution then the conductivity of dilute part decreases; thus the resistivity of electro dialysis system will increase. The results given in this study are in agreement with literature.⁷⁻¹²

As shown in Table 1, the value of conductivity decreases in cathode compartment for all samples, in comparison with feed wastewater, due to Cu^{2+} transport from the central compartment to cathode compartment and then to the copper electrodeposition reaction on the lead cathode surface. The values of conductivity in anodic compartment increase in comparison with feed wastewater. This can be due to a decrease in the solution resistance and also an increase of the diffusion constant through the ion exchange membranes. Also, increasing the value of conductivity in this compartment can be due to the oxygen formation. In the central compartment for almost all values of Cu^{2+} concentration, the value of conductivity decreases in comparison with feed wastewater. This indicates that the Cu^{2+} and SO_4^{2-} ions were removed from this compartment. Similar results are reported in our previous works.^{2,5}

In Table 1 are shown the values of temperature, measured after 3 h of treatment. It can be seen that the value of temperature enhances with the increasing of the concentration of solution, may be due to the augmentation of the resistance of system. Increase in temperature leads to a decrease in current efficiency. This is explained by the fact that an increase in temperature leads to broadening the membrane pores and thus to a decrease of the electrical resistance, but at the same time accelerates inclusion of ions in membrane structure, reducing the efficiency of current. These higher temperatures determined higher ion diffusivities, higher electrolyte conductivities, decreased electrical resistances for anolyte and catholyte and enhanced mass transport.

Table 1

The values of pH, conductivity and temperature for different concentration of copper ions and various flow rate

Flow rate, mL/min	Samples	Cu ²⁺ concentrations, g/L								
		1			2			4		
		T, °C	λ , mS/cm	pH	T, °C	λ , mS/cm	pH	T, °C	λ , mS/cm	pH
0	feed wastewater	22	27	1.35	22	40	1.21	22	70	0.98
4.2	anode compartment	27.5	36	1.28	28.4	38	1.21	31	116	0.95
	central compartment	27.9	20	1.39	29.6	31	1.14	32.8	70	0.93
	cathode compartment	28.5	12	1.62	29.9	24	1.38	32.1	62	1.23
6.6	anode compartment	24.3	38	1.21	29.4	58	1.04	29.8	96	0.91
	central compartment	25.5	25	1.42	30.4	35	1.19	31.1	65	0.96
	cathode compartment	25.8	18	1.58	29.9	31	1.31	31	60	1.18

In most studies the separation process was improved with increasing concentration of feed solution due to the presence of a sufficient quantity of ions adjacent to the membrane surfaces.^{7,8,10,11,14,16} Increasing the temperature improved the diffusion rate and so the recovery of metals. At the same time high temperature, H₂ evolution can cause depolarization effects that may reduce the electrodeposition rate of metal on cathode.

The mass flow, percent extraction and energy consumption

The amount of copper deposited on the lead cathode, evaluated in terms of mass flow (J_{mass}), the efficiency of electrodialysis cell, evaluated in terms of *percent extraction* (PE) and the energy consumption (EC) related to the amount of desired ionic species which are transferred through the ion exchange membranes are summarized in Table 2.

One may notice, from Table 2, that the values of J_{mass} , obtained for cathode compartment and different concentration of solutions, after 3 h, increase with increasing the concentration of copper ions. At low concentrations (1 g/L), the values of the J_{mass} are lower, due to the decreased motive force and also to the transfer capacity of the membranes that increases the time of transfer through the anion and cation exchange membrane. Similar results are given in a previous study.² The values of the mass flow in the cathode compartment are higher; at higher copper ion concentrations and higher flow rate. The highest value of mass flow obtained was 180.98 g/m² h at

ion concentrations of 4 g/L and flow rate of 6.6 mL/min. The increase of the flow rate from 4.2 mL/min to 6.6 mL/min, in order to remove copper ions, decreases the concentration overpotential. The results also show that at higher flow rates (6.6 mL/min) the effect of polarization decreases more dramatically and causes an increasing in removal rates. The results given in this study are in agreement with literature.^{15,17-20}

Keun et. al.²¹ studied the influence of the flow velocity on removal rate of Zn²⁺ from model solutions using an electrodialysis system. They reported that an increase in the flow velocity led to an increase in the dialytic rate. This fact can be due to the fact that boundary layer between bulk liquid and the ion exchange membranes thinned resulting in an enhancement of ion diffusion rate.

It was observed from Table 2 that the PE, for cathode compartment and different concentration of solutions, after 3 h, increases with the augmentation of the initial concentration of copper ions in feed solution, due to the increased flux of copper ions. On the other hand, the total time of the process increases with increasing the copper ions concentrations. Also the augmentation in copper ions concentration leads to the increase of the percent extraction of copper ions because the electrical resistance of feed solution decreases.

In most studies the PE increased with increasing feed concentration due to the presence of a sufficient quantity of ions adjacent to the membrane surfaces. Also, the high initial concentrations will influence the quality of the dilute stream.^{7,8}

Table 2

The values of mass flow, in cathode compartment, percent extraction and energy consumption, after 3 h of electro dialysis process

Cu ²⁺ concentrations, g/L	4.2 mL/min			6.6 mL/min		
	J _{mass} , g/m ² ·h	PE, %	EC, kWh/m ³	J _{mass} , g/m ² ·h	PE, %	EC, kWh/m ³
1	28.80	56.55	150.40	32.88	64.54	121.72
2	72.46	71.09	251.20	73.60	72.20	230.43
4	168.25	82.52	525.08	180.98	88.75	562.08

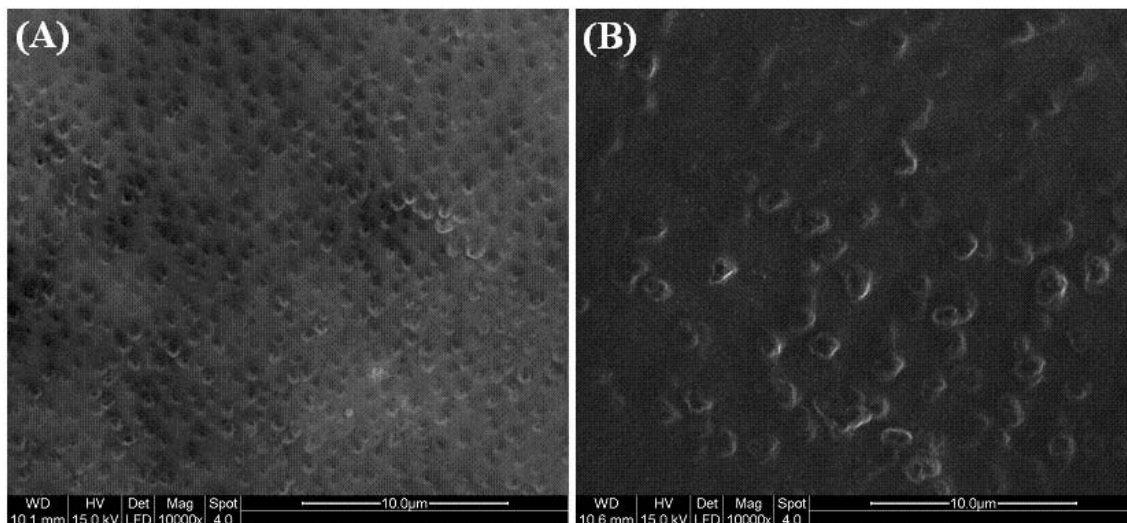


Fig. 1 – ESEM images of ion-exchange membranes: (A) Purolite A500 and (B) Puropack PP100.

The electro dialysis cell performance increased with increasing of initial concentration solutions and with enhancing of flow rate, at constant voltage; the PE of copper ions was greater (>88 %) at higher concentration of copper ions (4 g Cu²⁺/L). The values obtained for the removal of copper ions confirm the possibility of reuse of copper from these solutions.

Table 2 shows that the value of EC, calculated for electro dialysis system, with the total volume of 144.12 cm³, after 3 h of treatment, increases with increasing value of concentration of copper ions and this may be due to the higher current flowing through the electro dialysis cell. Also, it was obtained that the EC increased when the copper concentration in the solution was increased due to the increased transport rate of copper.

The EC values obtained were lower in the case of using lower concentrations (121.72 kWh/m³ at 6.6 mL/min and 1 g/L, after 3 h); this might be the result of the reduction of stack resistance. The EC values obtained were higher in the case of using higher concentrations (562.08 kWh/m³, at 6.6 mL/min and 4 g/L, after 3 h). This result can be explained by the fact that augmentation of the initial copper concentration, leads to an increase of current density which results in an increase in

energy consumption as was proposed in.²² These results are in agreement with those obtained by Ögütveren *et al.*,²³ in the removal of copper ions from wastewater by electro dialysis using IonacMA3475 anion and Nafion423 cation exchange membranes, respectively. They obtained a value of EC over 125 kWh/m³ at 40 V, at the concentration of 100 mg/L Cu²⁺, after 150 min. Ahmed *et al.*⁸ reported that the operation at pH<3 resulted in excessive energy consumption due to the increasing current associated with low pH.

Increasing the applied voltage over the limiting value (9 V) is not convenient in this study due to the occurrence of disadvantages such as membrane burning, electrolysis on the electrode plate, and high EC, which eventually increase the total cost. Also, the lower value of energy consumption might be obtained if larger numbers of membrane pairs are used. So, in this method one has to choose between working at higher removal rate or at lower energy consumption.

Morphology of ion exchange membrane

The ESEM micrograph (see Fig. 1) shows particles which appear on the membrane surface. At the same time ESEM also confirm the

uniformity of the membranes. The aspect of the ESEM micrographs indicates the occurrence of phase-inversion of the polymer solution. The difference in the pore size between the 2 membranes could be related with differences in anion (Purolite A500) or cation exchange resins (Puropack PPC100) particle size but also to the differences in the driving force for phase separation.^{4,24}

EXPERIMENTAL

Materials

Copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were purchased from Chimpar Bucharest. Sulphuric acid (98%) and Dimethylformamide (DMF) was purchased from Merck Millipore and Sigma-Aldrich respectively. All chemical were of analytical grade.

Membrane sample preparation

The membranes were prepared from a mixture of 10 % acrylonitrile-vinyl acetate- α methyl styrene copolymer solution in dimethylformamide (DMF) as solvent, by dissolving at 70°C during 3 h, in the presence of 5% ion exchange resin (Purolite A500 and Puropack PPC100) (Purolite Company). The polymer solution was cast onto a glass plate. The draw-down technique was used to produce films of wet thickness of 200 μm . Then, the glass plate with the polymer solution film was immersed in a bath of distilled water. By keeping in the water, membranes detach from the glass plate.

Electrodialysis cell

The electrodialysis cell (home-made, PVC) consisted of three detachable circular compartments, a DC power supply (Protek, Germany) (30 V, 5 A), two working lead electrodes, a

peristaltic pump with four independent controllable channels (Ismatec, USA, Model MS-CA4/640, Click'n'go cassettes, 6 pump rollers, 40 rpm) and three reservoirs. The three tubes types Taygon were used for recirculation of solution from each compartment. The experimental equipment used for electrodialysis is shown schematically in Fig. 2.

The total volume for all compartments electrodialysis cell was equal to 144.12 cm^3 (48.04 cm^3 /compartment). The cell was separated by anion- and cation-exchange membranes with an effective area of 28.26 cm^2 , placed in the cell by rubber gaskets. The working electrodes were effective area of 28.26 cm^2 and are arranged in parallel.

Cycle-mode electrodialysis was accomplished at constant applied voltage imposed between electrodes by a power supply (Protek, Germany) of 9 V, at different controlled flow rate (6.6 and 4.2 mL/min), at room temperature and the operation time was 3 h for each experiments. The current intensity was between 0.60 A – 3.42 A. The solutions from compartments (anode, central and cathode) flowing from their respective holding reservoirs were pumped and entered the electrodialysis stack. After that, the streams were recycled to their holding reservoirs, for 3 h.

A control sample electroplating solution containing Cu^{2+} ions with concentration between 1 – 4 g/L, was prepared by dissolving copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and sulphuric acid 98% (molar ratio 1:1) in distilled water.

Characterizations

The pH and conductivity measurements of all solutions were performed using a Hanna Instruments HI 8915 pH-meter and a WA-100 ATC (Votcraft, Germany) conductometer, respectively. The conductometer contains a temperature sensor that allows the automatic compensation of temperature.

Concentration of Cu^{2+} was determined by titration method, according to a procedure detailed in reference.²

Morphology surface of anion- and cation-exchange membranes were visualized using *Environmental Scanning Electron Microscopy (ESEM)* using a FEI-Quanta 200 microscope. The ESEM images were obtained in low vacuum mode.

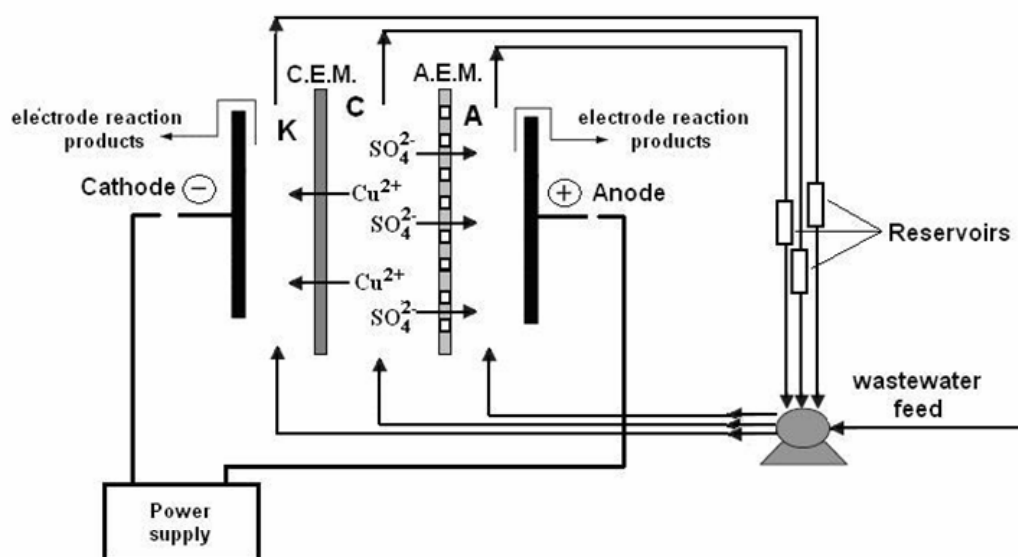


Fig. 2 – Schematic diagram of the electrodialysis cell; A.E.M – anion exchange membranes, C.E.M. – cation exchange membranes, K – cathodic compartment, C – central compartment, A – anodic compartment.

The mass flow (J_{mass}) was calculated using following equations:²

$$J_{\text{mass}} = \frac{\Delta C \cdot \Delta V}{A \cdot t} \quad (1)$$

$$\Delta C = C_0 - C_f \quad (2)$$

where: J_{mass} – mass flow, $\text{g/m}^2\text{h}$; A – effective working area of the lead electrode, m^2 ; ΔV – initial volume of solution from each compartment, L ; ΔC – variation of the solution concentration, g/L ; C_0 – initial concentration of electrolyte solution, g/L ; C_f – final concentration of the solution after three hours of experiment, g/L ; t – working time, h .

Percent extraction of Cu^{2+} was calculated by the following relation:^{2,5,7,16-20}

$$PE = \frac{C_0 - C_f}{C_0} \cdot 100 \quad (3)$$

where: C_0 – initial concentration of electrolyte solution, g/L ; C_f – final concentration of the solution after three hours of experiment, g/L

The energy consumption (EC) can be expressed by the equation:^{8,9,16}

$$EC = \frac{\int_0^t I \cdot dt}{V} \quad (4)$$

where: EC is the energy consumption (kWh/m^3), E is the applied potential (V), I is the current passing through the electro dialysis system (A), t is the time (h), and V is the initial volume of the cathodic compartment (m^3).

CONCLUSIONS

It was found in our work that de removal of Cu^{2+} from wastewater, at various conditions can be carried out successfully using electro dialysis with ion exchange membranes. The PE of copper ions depends on the concentration of the solution to be treated and flow rate. It was found that the PE is greater (>88 %) at higher concentration of copper ions ($4 \text{ g Cu}^{2+}/\text{L}$) and flow rate at 6.6 ml/min . The energy consumption for copper ion transport varied between 121.72 and 562.08 kWh/m^3 feed.

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