



## Factors Affecting Electrodialysis Unit Performance in the Removal of Copper from Wastewaters and Aquatic Environment Treatment

Kawthar A. Omran<sup>1,2</sup>, Mohamed E. Goher<sup>2\*</sup>, Amr S. El-Shamy<sup>2</sup>

<sup>1</sup>Department of Chemistry, College of Science and Humanities, Shaqra University, Saudi Arabia

<sup>2</sup>Freshwater & Lakes Division, National Institute of Oceanography, Fisheries (NIOF), Cairo, Egypt

\*Corresponding Author: [smgoher@yahoo.com](mailto:smgoher@yahoo.com) ORCID ID [0000-0001-9377-2429](https://orcid.org/0000-0001-9377-2429)

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### ABSTRACT

Wastewater treatment and removal of heavy metals are of great importance, especially in terms of industry, economy, environment and public health. Electrodialysis desalination mode is an effective process for treating metals in contaminated solutions and for further recovery of metals to new uses. In this work, the removal of copper ions from solution using a recirculating electrodialysis system was studied. Different factors affecting ED performance, such as applied voltage, pH, flow rate, and metal ion concentration on metal removal efficiency, energy consumption, and current efficiency were investigated. The stainless-steel 316 (SS 316) electrode was used as an anode and a cathode and has the advantage of a low corrosion rate. The optimum conditions for 99.59 % removal of 200 mg/L of copper in 60 min are 18 V, pH 4, and a flow rate of 800 ml/min to produce a dilute solution of 0.83 mg/L  $\text{Cu}^{2+}$  (<1.3 mg/L), which is within the acceptable limits and suitable for discharges into the environment. Additionally, the current efficiency was 87.78%, the flux was calculated to be 7.84  $\mu\text{mol}/\text{m}^2\text{m}$ , and the energy consumption was 1.73 Wh/L. The study shows that the electrodialysis method can be used efficiently for the removal of copper ions from wastewater.

### INTRODUCTION

Water cycle is disrupted due to the growing population growth, water needs and human activities. It became therefore necessary to act to preserve water resources, so that water quality would be available to all mankind. Moreover, rapid contamination of toxic metals (Guowei *et al.*, 2021) has devastating consequences for the population and ecosystems, affecting crops yield, livestock, and drinking water for human consumption (Duruibe *et al.*, 2007). One of the most harmful heavy metals is copper among the various pollutants. It is daily discharged into wastewater streams from various industries, such as electroplating, paints and dyes, petroleum refining, fertilizers, mining and metallurgy, explosives, pesticides and steel. In the population living near copper mining areas, epidemiological studies have found a positive association between copper mining activities and various health diseases (e.g., headaches, cirrhosis, kidney failure and even cancer) (Chen *et al.*, 2022). USEPA (2023) recommended 1.3mg of copper as the maximum contaminant level

goal (MCLG), which indicates that there is no known or expected risk to health in drinking water below this level.

In particular, metal species accumulate inside vital organs leading to short and long-term hazardous effects (JOHN *et al.*, 2002). Each day, a total of approximately 2 million tons of untreated industrial, sewage and agricultural waste are discharged into the surface waters (Sreenath *et al.*, 2019), and the volume is dramatically increasing with time (Qiaoqiao *et al.*, 2017). Even the treated domestic wastewater contains metals (Kangala *et al.*, 2003; Malwina *et al.*, 2019), and the treatment processes are often not optimized. The different compositions of influent wastewater can further adversely affect the treatment efficiency (Kangala *et al.*, 2003; Malwina *et al.*, 2019). The increase in demand for water has led to the development of new methods of wastewater treatment, such as ion exchange, membrane processes, solvent extraction, incineration & Adsorption)(Koubaissya *et al.*, 2011).

Desalination technology has become a major method of obtaining freshwater in many water-scarce regions (Jihong *et al.*, 2022). The desalination technologies can be divided into two main categories, evaporation and thin-membranes methods. The evaporation method is facing serious scaling and corrosion problems, while the thin film method has become the mainstream method for building plants internationally due to its low energy consumption and high recovery rate (Malalagama *et al.*, 2022). The membrane involving method is divided mainly into reverse osmosis (RO) and electrodialysis (ED) (Juve *et al.*, 2022). RO has disadvantages such as high requirements for water quality, low fresh water yield and easy scaling of membranes (Khoiruddin *et al.*, 2022). Electrodialysis (ED) is a membrane process, where the high electrical potential energy is used to separate cations and anions from the stream, and it is commercially used on a large scale for production of drinking water from water bodies and treatment of industrial effluents due to its energy efficiency, environmental adaptability and flexibility (Mehdi *et al.*, 2023). ED was originally conceived for seawater desalination. In ED system, ion exchange membranes are used, and ion is transported through ion selective membranes from one solution to another under the influence of electrical potential difference used as driving force. Electrodialysis has been widely used in the desalination process and recovery of useful matters from effluents. ED has the advantages of low requirements for pretreatment, convenient operation and maintenance, less chemical dosage, low energy consumption and long service life of the device and has certain advantages in high brine treatment (Nemati *et al.*, 2017). The performance of ED depends on operating conditions and device structures such as ion content of raw water, current density, flow rate, membrane properties, feed concentration and the geometry of cell compartments. The membrane is a selective interface characterized by two phases. Membranes can be made from inorganic, organic and metal polymer, and they are used for gas separation solid - liquid and liquid- liquid separation. Separation is depending on the membrane pore size.

In the same context, ED is an alternative membrane separation process used in wastewater treatment. In ED system, the ion exchange membranes are arranged between the anode and cathode. The ionic compounds in the feed water, using an

electrical driving force, start moving across ion exchange membranes. The cations in the solution migrate towards the cathode, and the anions migrate towards the anode via applying electrical current between the anode and cathode. The cations pass through the cation exchange membrane, but they are retained by the anion exchange membrane. Similarly, anions pass through the anion exchange membrane (AEM) but they are retained by the cation exchange membrane. A number of membrane pairs can be installed in parallel between a pair of electrodes to form a stack. The result of the process is the occurrence of concentrated and diluted compartments in the system. The electrolyte solution is used to ensure the conductivity and remove gases produced by electrode reactions in the system (**Strathmann et al., 2010**). Moreover, electrodialysis processes are one of the promising separation technologies for clean production. Given that raw materials have been witnessing decreases worldwide, ED system can provide recycling, reusing some valuable substances. For sustainable development, clean technologies have become more and more important. Electrodialysis can remove ions by electrical potential difference. Thus biomass, colloidal material or organic materials in the feed water will survive in the product stream (**Oztekin et al., 2016**). In the removal of  $\text{Cu}^{2+}$  from working solutions, electrodialysis has been proven to be highly effective (**Liu et al., 2023**). For example, the removal percentage of ~97% has been attained under optimum conditions for copper in the study of **Mohammadi et al. (2004)**. ED is capable of treating and recycling rinsing water from baths and rinse solutions from cyanide electroplating (flowing through concentrate and dilute compartments, respectively) (**Korngold et al., 1978**) as well as from electroless plating (**Mohammadi et al. 2004**). In addition, electrodialysis exhibits high selectivity in separations and high energy efficiency at high operating costs (**Chiapello et al., 1992**).

In the present study, a special electrodialysis cell was designed to remove copper ions from wastewater using cation membranes (Fumapem F-930-RFS00) and anionic membranes (Pention-AEM-72-05-5% crosslinking) through batch recirculation mode in ED process. The effects of several parameters, including applied voltage, pH of the feed solution, initial concentration of the copper solution, and the flow rate of dilute and concentrate solutions were examined to study the optimum conditions for ED cell performance. Additionally, the current study aimed to obtain a dilute solution of acceptable concentration for copper ( $< 1.3 \text{ mg/L}$ ) under the optimum condition from the point of view of high current efficiency and low energy consumption. Moreover, producing a highly concentrated solution in the concentrate compartment suitable for further recovery of copper was an additional target.

## MATERIALS AND METHODS

### Chemicals and preparations

Chemicals of high purity ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , NaCl, NaOH, HCl) were purchased from Sigma-Aldrich Chemical Companies. The solutions of salts were prepared using deionized water ( $\text{EC} < 1 \text{ }\mu\text{S/cm}$  and  $\text{pH } 5.8 \pm 0.1$ ). A suitable volume of copper stock solution was prepared by dissolving calculated quantities of copper (II) sulfate pentahydrate in deionized water. The pH adjustments were done by 0.1 M NaOH and 0.1 M HCl (APHA, 2005), using a pH meter (Ion Analyzer 399A, Orion Research,

Cambridge, MA, USA). Copper metal in solutions was determined by an AA-7000 SHIMADZU atomic absorption.

### Ion exchange membranes

Ion-exchange membranes were arranged in the way of obtaining four separated streams. Pention-AEM-72-05-5% crosslinking ion exchange membranes were produced in FUELCELL-USA AEM (2 anion membranes) and Ralex® Membrane CMHPP – Mega- EU, Czechia CEM (3 cation membranes) were used; their main properties are mentioned in Table (1) according to the supplier.

**Table 1.** RALEX ion exchange membranes properties

	Material Ion-exchange groups	Binder	Thickness (µm) Dry	Permeability selectivity (%)	Resistance (Ω cm <sup>2</sup> )	Counter ion transference number	Ion Exchange capacity meq/g)
AEM	R-(CH <sub>3</sub> ) <sub>3</sub> N <sup>+</sup>	Matrix poly(norbornene)	10	90-100	<4.2	0.95	3.4-3.6
CEM	R-SO <sub>3</sub> <sup>-</sup>	Cross-linked Polystyrene	450	90	<8.5	0.95	2.2

### Description of ED set-up technique

An electrodialysis (ED) cell was designed to treat the capacity of a 12L solution containing 200mg/ L of copper ions. The experimental setup is shown schematically in Fig. (1). The stack contains the following key parts: electrodes [cathode (-) and anode (+)], low-density polyethylene spacers, anionic exchange membranes (AEM), cationic exchange membranes (CEM), 4 pumps USA GRUNDFOS (10L/ min), a rectifier A.M with an automatic range of 0–70 V and 0–20A flow meters (100 – 2000 ml/min) in addition to 3 tanks for electrolyte solution (2 L), concentrate solution (6 L) and dilute solution (12 L). The ED unit that was used in the lab experimental scale has 2 pair cells with 2 CEM and 3 AEM, where the third anionic membrane was located close to the cathode to protect it from damage by blocking the pass of copper ions to the cathode. The total volume of the ED unit was equal to 0.018m<sup>3</sup>, supplying an activated membrane area of 0.04 m<sup>2</sup> in each room. The temperature of the solutions is adjusted using a reservoir thermostatic bath. Pre-the batch experiment; to complete the set-up of the ED unit, the material of electrodes and electrode arrangements were tested to achieve the best stability, continuity of the ED unit and the highest removal efficiency.

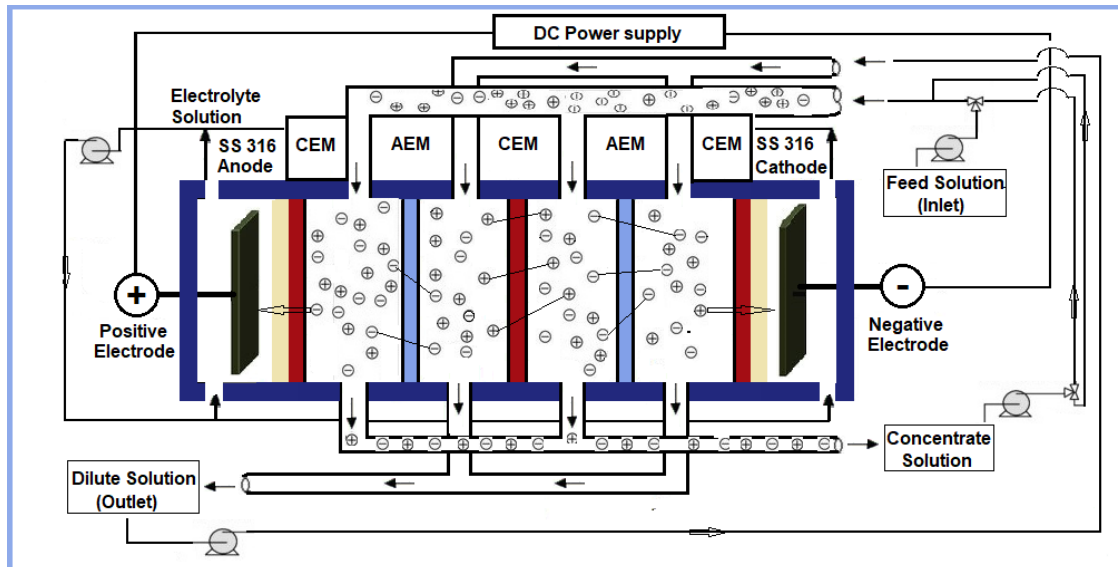


Fig. 1. Schematic diagram for parts of ED unit

### Process sequence and batch experiments

Starting the current over the stack, the cations and anions are attracted towards the cathode and anode, respectively. They reach a membrane, some could pass and others are rejected, depending on their size, charge and hydrophilic effects. At the same time, water molecules pass through the membrane as a solubility shield for ions, and flow occurs between the membranes (Koutsou *et al.*, 2007; Silva *et al.*, 2013). In general, the positive ions ( $\text{Cu}^{2+}$ ) are attracted to the cathode and pass through the CEM. In the same manner, the negative ions ( $\text{SO}_4^{2-}$ ) are attracted to the anode through the AEM. In both cases,  $\text{Cu}^{2+}$  is stopped by AEM and  $\text{SO}_4^{2-}$  is blocked by CEM. Consequently, the concentration of  $\text{Cu}^{2+}$  or  $\text{SO}_4^{2-}$  is increasing in one chamber which is known as the concentration chamber, and its stream is known as the concentrate solution. In contrast, the concentrations of ions are decreasing in the adjacent chamber, which is known as the dilute chamber, and its stream is known as the dilute solution.

In the present study, the batch recirculation mode was performed to indicate the optimum conditions of ED operation. The study was carried out under different factors including applied voltage (3-30 V), initial concentration of copper (10 – 400 mg), pH (3-6), and flow rate of feed solution (200-1200 ml/min). The effect of the studied factors on the current efficiency, energy consumption, and removal efficiency is examined, where the optimum conditions that achieve the highest removal efficiency and current efficiency and lowest energy consumption. The solution of electrolyte (2 L of 3 - 4 mM NaCl) was circulating in a closed cycle between the electrode's chambers.

### Data analysis

The removal efficiency, energy consumption, and current efficiency were calculated to see how the experimental parameters affect the performance of the ED system in quantitative terms.

- The removal efficiency (RE) is a parameter that determines how much of the heavy metal in the wastewater that enters the ED cell is removed at the end of the experiment.

$$RE (\%) = \frac{(C_o - C_t)100}{C_o}$$

Where, RE is the removal efficiency %;  $C_o$ : the initial feed concentration of dilute solution (mg/L), and  $C_t$  is the outlet concentration of dilute solution at time t (mg/L).

- The energy consumed (EC) in an electro dialysis cell is proportional to the applied volts, time, the intensity of the current and the volumetric amount used. The experiment's time is measured in minutes, and the applied current is measured in amps.

$$EC = \frac{(W * t)}{V_d}$$

Where, EC is the energy consumed (Wh/L) or specific energy consumption,  $W = V \times I$  (W is the electrical power (watt); V is the difference of electrical potential ( applied voltage, Volt); I is the electrical current (Amper), T is the time in hours (h), and  $V_d$  is the volume of the dilute solution (L).

- Current efficiency (CE) is an important parameter in determining the ED system's optimal range of applicability. The current efficiency also shows how effectively the ions are transported by the applied current during the ED process (Sadrzadeh & Mohammadi, 2009).

$$CE (\%) = \frac{zF V_d(C_o - C_t)100}{Nit}$$

Where, CE is the current efficiency %; Z is the charge of the ion transported (2 for Cu); F is Faraday constant (96485 C/mol);  $C_o$  is the initial feed concentration of dilute solution (mol);  $C_t$  is the outlet concentration of dilute solution at time t (mol); t equals the time in second (s); N: the number of cell pairs in the ED stack (2 in the present study), and I: electrical current (A).

- The molar flux is the amount of matter (electrical, molar or volumetric) passing through a given area in a given time is referred to as flux. Flux is another critical parameter for comparing ED cell efficiency (Arar *et al.*, 2014); It can be calculated via the following equation:

$$J = \frac{1000(C_o - C_t)}{NA t}$$

Where, J is the molar flux ( $\mu\text{mol}/\text{m}^2 \text{ m}$ );  $C_o$  is the initial feed concentration of dilute solution (mol);  $C_t$  is the outlet concentration of dilute solution at time t (mol);  $V_d$  is the volume of the dilute solution (L); A is the effective membrane area ( $\text{m}^2$ ); t is the time in minutes (m); I is the electrical current (A); N= the number of cell pairs in the ED stack (2 in the present study), and 1000 stands for the factor of ( $\text{mol}/\text{m}^2 \text{ m}$ ) to ( $\mu\text{mol}/\text{m}^2 \text{ m}$ )

## RESULTS AND DISCUSSION

The purpose of the study was to choose the most practical operating parameters in order to optimize the process by examining the performance of ion exchange

membranes under various process conditions. The treated model wastewater should be non-toxic or even acceptable for discharge into the environment under these optimal conditions (**Czech Government, 2003**). Additionally, the treatment method is distinguished by its high current efficiency (CE) and low energy usage (EC). The applied voltage, flow rate of the concentrate and dilute solutions, pH, and initial metal content in the feed are the objective parameters whose effects were taken into account.

### Electrode materials and arrangements

An electrochemical cell was designed, possessing a cathode and anode from some materials to choose the suitable electrode material that is more stable in our ED cell, which was prepared to treat heavy metal- contained solution. Table (2) provides the details of the corrosion rate of electrodes due to the cyclic voltammetry (CV) through a continuous process of treatment with 200mg/ L copper solution for 24h under conditions of 30 V, pH 4, and a low flow rate of 100ml/ min for feed solutions at 25°C. The connection of electrodes with the power supply was reversed every 6 hours for 5min to regenerate the removal process, prevent the membrane contamination and reduce the concentration polarization. During the reverse process, the ED unit was used as a closed system by stopping the flow and the exit of the solution. The electrodes used had a constant dimension of 150\*150\*3 mm and different weights of 540, 600, 493, and 142 g for stainless steel 316 (SS316), copper, tin and graphite electrodes, respectively. Table (2) shows that the SS316 material is proven to be very excellent as a cathode and anode because of having a decreased corrosion rate in comparison to the other examined materials.

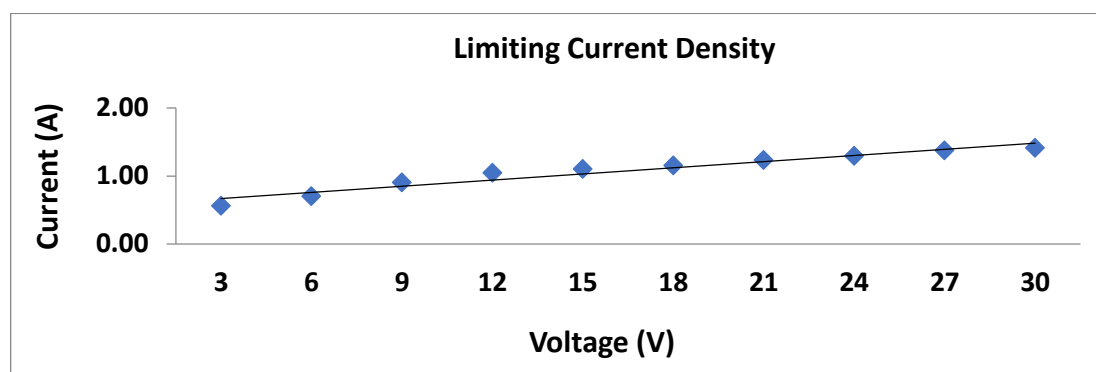
**Table 2.** The corrosion rate of electrode materials

No.	Electrode material	Anode weight (g)	Loss of anode (g)	Loss of anode % x 10 <sup>-5</sup>	cathode weight (g)	Loss of cathode (g)	Loss of cathode % x10 <sup>-5</sup>
1	Copper/SS316	600	0.979	163.2	540	0.023	4.3
2	Tin/SS316	493	1.1	223.1	540	0.025	4.6
3	Graphite/SS316	142	0.16	112.7	540	0.022	4.1
4	SS316/SS316	540	0.1	18.5	540	0.013	2.4
5	Copper/Tin	600	0.725	120.8	493	0.45	91.3
6	Copper/Graphite	600	0.35	58.3	142	0.19	133.8

On the other hand, the arrangement of electrodes to the CEM and AEM was tested to adjust the best distance between the electrodes and the ion exchange membrane, which gives the highest removal efficiency. In this experiment, the ED unit with two SS316 electrodes at the anode and cathode was used to treat 200mg/ l copper solution under the same conditions mentioned above for the test of the performance of the electrode material. The removal efficiency of Cu was 79.79, 64.50 and 57.47 % for the 2, 4 and 6 cm arrangement of electrodes, respectively. These results indicate that fixing the electrodes (anode and cathode) at a distance of 2 cm from the membranes is the best distance to increase the removal efficiency.

### The effect of applied voltage

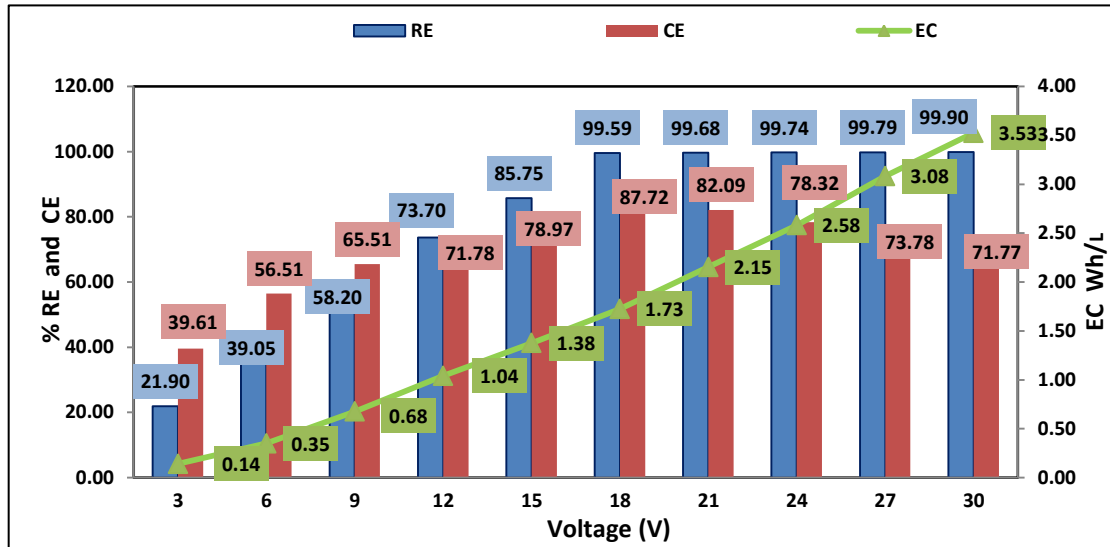
In this study, the potentiostatic mode has been particularly selected instead of galvanostatic mode to operate at constant voltage, avoiding the changes of the high voltage values at the low concentration of dilute solution in the stack (**Parulekar, 1998; Dmirciog *et al.* 2001**). Firstly, to determine the limiting current density (LCD), a voltage of range 0 - 30 volts was separately applied to 200mg/ l  $\text{Cu}^{2+}$  solution at pH 4. Every 10 minutes, the voltage was increased by three units, and current values were recorded. One of the crucial components of the electro dialysis system principle is the LCD. It offers details on the electrical resistance and current. As there are already a lot of ions present when the experiment starts, once the voltage is applied, the current begins to increase and ion migration occurs. The moment the system achieves the limiting current density is the point at which ion migration no longer takes place. In this situation, even if the voltage is increased more, there is no longer any ion movement, and the current stabilizes (**Senem Kırmızı *et al.*, 2023**). Fig. (2) shows the linear relationship between current density and the voltage obtained indicating that the current-voltage curve is in the ohmic region and the current density does not reach the LCD on the range of 0-30 V applied voltage for this ED cell.



**Fig. 2.** Limiting current density; current-voltage curve

The effect of applied voltage on removal of 200 mg copper/ L aqueous solution was investigated at cell voltages of 3, 6, 9, 12, 15, 18, 21, 24, 27 and 30 V under conditions of a flow rate of 800ml/ min, pH 4, 25°C and for a retention time of 60min. Fig. (3) and Table (3) show the variation of RE, CE and EC at the different applied voltages. The increase of the removal efficiency from 41.0 % to 99.59 % at 3 and 18V, respectively, was noticed. While, a slightly increase of RE was observed at increase of the applied voltage to 30V, recording 99.9 %. In the same contest, the CE increases from to 39.61 % at applied voltage 3 to 87.72 % at 18V; the further increase of the applied voltage is accompanied by a decrease in the CE to reach 71.77 % at 30 V. On the other hand, the rate of energy consumption increases steadily with increasing voltage to record 0.14, 1.73 and 3.53Wh/ L at 3, 18 and 30 V, respectively.



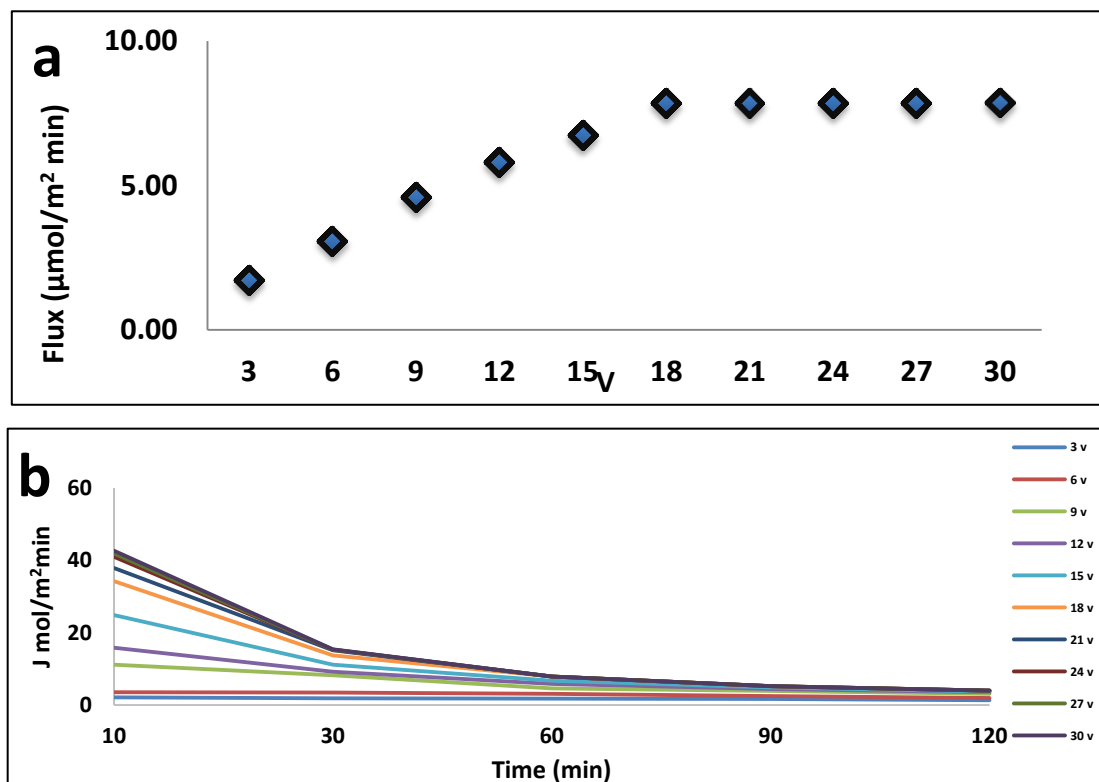


**Fig. 3.** The effect of voltage on RE, EC and CE for Cu (II) ( $t= 60\text{min}$ ;  $C_i= 200\text{mg/L}$ ;  $\text{pH}= 4$ ;  $\text{Fr}= 800\text{ml/min}$  at  $T 25^\circ\text{C}$ )

**Table 3.** Effect of voltage on RE, EC and CE for Cu (II) through 120min ( $C_i= 200\text{mg/L}$ ;  $\text{pH}= 4$ ;  $\text{Fr}= 800\text{ml/min}$  at  $T 25^\circ\text{C}$ )

V (volt)	Time (min)	RE %	CE %	EC (Wh/L)	V (volt)	Time (min)	RE %	CE %	EC (Wh/L)	
3.00	10.00	4.45	6.53	0.10	18.00	10.00	72.60	54.88	1.55	
	30.00	11.90	19.13	0.12		30.00	87.04	68.88	1.64	
	60.00	21.90	39.61	0.14		60.00	99.59	87.72	1.73	
	90.00	31.20	65.84	0.16						
	120.00	34.40	84.99	0.17						
6.00	10.00	7.44	12.77	0.30	21.00	10.00	80.20	57.21	2.03	
	30.00	21.60	26.05	0.32		30.00	95.78	74.06	2.10	
	60.00	39.05	52.05	0.35		60.00	99.68	82.09	2.15	
	90.00	46.65	67.51	0.38						
	120.00	48.80	77.24	0.61						
9.00	10.00	23.60	22.99	0.59	24.00	10.00	86.68	61.83	2.38	
	30.00	52.25	53.46	0.62		30.00	96.91	71.65	2.48	
	60.00	58.20	62.72	0.68		60.00	99.74	78.32	2.58	
	90.00	74.15	83.46	0.71						
	120.00	78.05	95.26	0.74						
12.00	10.00	33.45	29.72	0.91	27.00	10.00	88.69	60.70	2.90	
	30.00	58.15	54.04	0.96		30.00	97.45	70.01	3.02	
	60.00	73.70	71.78	1.04		60.00	99.79	73.78	3.08	
	90.00	84.75	89.43	1.09						
	120.00	88.92	97.91	1.14						
15.00	10.00	52.55	43.99	1.28	30.00	10	90.40	60.24	3.30	
	30.00	70.70	61.74	1.30		30.00	97.62	66.81	3.43	
	60.00	85.75	78.97	1.38		60.00	99.90	71.77	3.53	
	90.00	93.30	90.87	1.45						
	120.00	95.10	94.44	1.51						

The number of ions transported across the membrane is proportional to the current density or the electric current. As the voltage increases, the current density also increases. Increasing current density is accompanied with an increase in the number of transported ions, i.e., the flux. Therefore, it is expected that metal ion removal will increase with time and with increasing voltage (Senem Kirmızı *et al.*, 2023). In the ED cell, it has been discovered that current efficiency decreases after a voltage value of 18V. Considering the energy consumption, a consistent increase in voltage was observed. Low energy consumption, high current efficiency and high removal efficiency are required in separation systems in terms of cost. As a result, 18 volts for copper removal satisfy all requirements. As the voltage value increases, the energy consumed increases aligned with the current's increase. Many studies, including those of Kabay *et al.*(2008), Abou-Shady *et al.* (2012), and Gherasim *et al.* (2014) postulated that upon the increase in voltage, energy consumption increases. In addition to low energy consumption, high current efficiency is also critical. As the voltage value increases, the ions are transported at a faster rate due to the increase of current. As the flux for copper ion increases with the voltage value, it is expected that the amount of flux will increase due to the ion transfer to the cathode compartment. No decrease in flux was recorded because the LCD was not reached. The flux variation for different voltage values of ED cell of removing 200mg/ L of Cu solution is shown in Fig. (4a). Obviously, the flux increased with the voltage's increase till a value of 18 V. However, after reaching the optimum value, the flux values were nearly constant. The increased flux due to the increase in voltage can be attributed to the increase in driving force due to ion migration.



**Fig. 4.** (a) The variation of molar flux with voltage ( $C_i = 200\text{mg}/\text{L}$ ,  $\text{pH} = 4$ ,  $\text{Fr} = 800\text{ml}/\text{min}$  at  $T = 25^\circ\text{C}$ ) (a) and (b): The variation of molar flux with time and voltage ( $C_i = 200\text{mg}/\text{L}$ ,  $\text{pH} = 4$ ,  $\text{Fr} = 800\text{ml}/\text{min}$  at  $T = 25^\circ\text{C}$ ).

In the applied voltage range (3-30 V) of the experimental work, the limiting current density was not reached, so the flux (transfer of anions and cations) increases with the voltage's increase. Fig. (4b) indicates that, at the start of the process, the flux at the high applied voltages was much more than that at the low voltages. The increase of voltage increases the driving force due to the ion migration, and therefore, the flux increases with the voltage's increase. Furthermore, at the beginning of the experiment where the lowest resistance with large amounts of ions is available, the maximum rate of ions moving to the electrodes (i.e. the highest flux) is achieved. As the concentrations of the ions in the diluted solution decline over time, the migrations of ions to the electrodes also decreases, and the flux eventually reaches its lowest point. In addition, after 10 minutes, the flux values of the high voltage (18-30) were near to one another, but at the end of the experiment, the flux values of all the applied voltage (3-30 V) were quite close to one another (Fig. 4b).

### The effect of pH

The pH of the feed solution is an important parameter in the ED stack. A very low pH value solution is very acidic and can expect a competitive transfer across the membrane between the metal cations and protons (Gering & Scamehorn, 1988). While at higher pH, many metals may be precipitated. Therefore, choosing the appropriate pH range in the metal removal process in the ED stack is sensitive and of great importance to achieve the greatest ED operating efficiency. In our study, the pH range of 2-6 was tested to detect the favorable pH value of the best copper removal performance in the designed ED unit. Fig. (5) shows that the removal increased with the increase of the pH value from 2 to 4, which recorded the maximum removal and then decreased with the increase of pH value. The difference in the removal with pH change may be a result of hydrogen ions' changes. With the increase in pH from 2 to 4, the amount of removal, current efficiency, and energy consumption increased over time. In general, the pH value changes with time for each pH value, so the ion mobility in the medium affects the energy used and the current efficiency. The conductivity of the solution was high at the low pH values due to the excess of  $H^+$  in the medium causing the increase of current and hence the increase of EC. Whereas, the increase of the current under constant voltage increases the amount of energy used and decreases the CE.

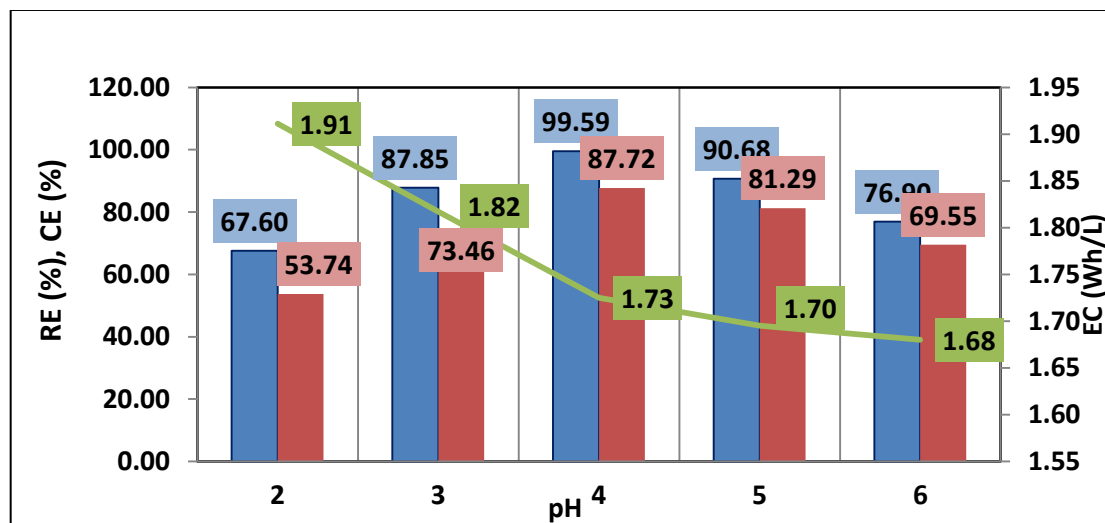
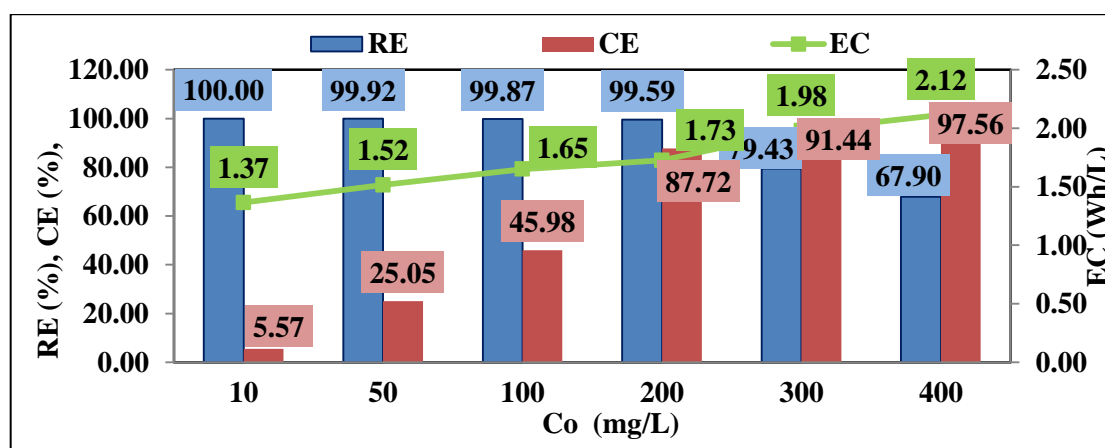


Fig. 5. The effect of pH on RE, EC and CE ( $t = 60$  min,  $C_o = 200$  mg/L,  $F_r = 200$  mL/min, Voltage = 18 V at T of  $25^\circ$  C).

At low pH, the lowest CE value was found, which is related to the increase in acidity and the amount of hydrogen ions, which use the majority of the current (Gherasim *et al.*, 2014). Moreover, the  $\text{Cu}^{2+}$  competes with the  $\text{H}^+$  at low pH values and the rate of removal is reduced, where the mobility of  $\text{H}^+$  (3.756) is much higher than that of  $\text{Cu}^{2+}$  (0.288), and it is easier to pass through the membrane as the pH decreases (Li *et al.*, 2021; Kreysa *et al.*, 2014). The pH (4) value shows the highest RE and CE and the lowest EC thus it is the most appropriate pH value. The removal decreased after reaching the optimum value of pH 4. Despite the low energy consumption at pH values of 5 and 6, pH 4 was the most appropriate value due to the high difference in the removal and current efficiency.

### The effect of initial concentration

The effect of initial metal concentration in feed is of great importance in order to assess the optimum domain of applicability of the ED process investigated, and thus performing highly effective ED process. Varied initial copper concentrations (10–400 mg Cu/L) in the feed solution were used to investigate the influence of initial metal concentration on the ED effectiveness through the recirculated batch mode. The applied voltage and pH were adjusted to the values previously observed as optimal for this process, i.e. 18 V and pH 4, while the flow rate was regulated in 800ml/ min, and the experiment is performed for 60min at 25°C. Fig. (6) shows that a decrease in removal efficiency, an increase in the current efficiency and energy consumption are observed as the concentration increases. This is attributed to the abundance of Cu (II) ions in the medium. The high current efficiency also shows the large number of ions present in the medium. The ions carry the current, hence its efficiency is also high. In addition, the increase in concentration indicates an increase in conductivity, but the removal efficiency decreased despite this increase. Likewise, concentration polarization can help reduce the removal efficiency. The limited separation capacity of the membranes can also affect this situation.

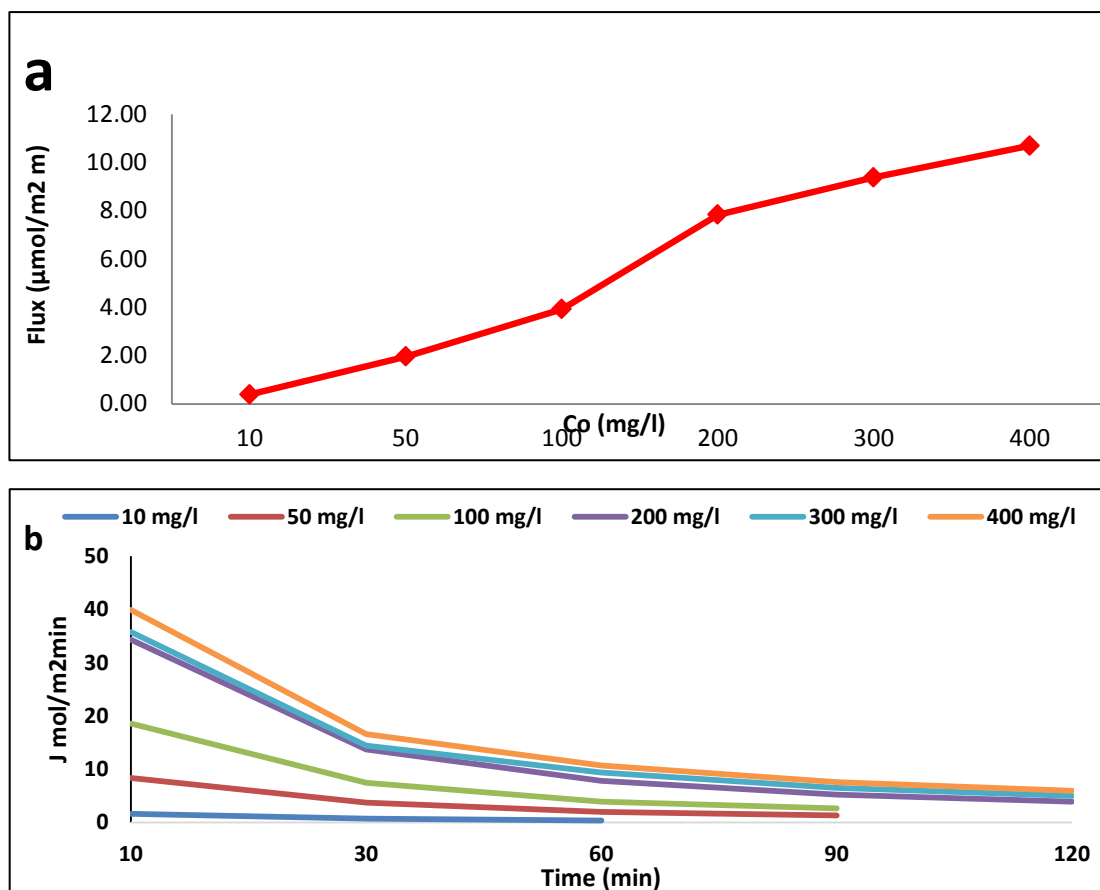


**Fig. 6.** The effect of initial metal concentration on RE, EC and CE ( $t = 60\text{min.}$ ,  $Fr = 200\text{ mL/min}$ , Voltage= 18 V, pH 4 at T 25°C)

With increasing concentration, excess ions can create resistance causing pollution. In this case, the ED cell will have an adverse effect, resulting in

accumulation and stratification in the membranes, and the removal efficiency will decrease (**Sadrzadeh et al., 2008**). In **Senem Kirmızı (2023)** study on Cr (VI) and Ni (II) removal by the electrodialysis method with a batch recycle, it is seen that the removal efficiency is much higher at low concentrations, regardless of the type of ion [30]. It is noted that, at using 200mg/ L of  $\text{Cu}^{2+}$  as initial concentration, a high removal efficiency (99.59 %), a high current efficiency (79.43 %) and a low energy consumption (1.73 W/L) were observed, thus 200mg/ L of  $\text{Cu}^{2+}$  is the most appropriate value. Although a higher removal was recorded at initial concentration values of 10, 50 and 100mg/ L, the value of 200mg/ L was observed to be the most appropriate value due to the high difference in current efficiency. The RE decreased after reaching the optimum value of 200mg/ L and falls to 67.9% for 400mg/ L of initial concentration. With increasing concentration, the medium becomes dense with ions. Moreover, the current density increased with concentration. In this case, it is expected that the removal of these ions requires more energy than necessary. In many studies, an increase in energy consumption was observed with an increase in concentration (**Kabay et al., 2008; Gherasim et al., 2014**). Generally, the current efficiency increased as the concentrations of copper ion increased. In this case, the decrease in the electrical resistance of the solutions may have increased the current efficiency.

At high concentrations, ion removal is problematic, either due to excess ion concentration in the medium (more conductivity) or concentration polarization, but the efficiency decreases. Moreover, due to the ion abundance in the medium, the time was maintained for a long time to ensure removal, and besides, energy consumption increases. This is undesirable in both laboratory scale systems and industrial activities. In accordance with several studies, the test results indicate 100% removal efficiency is observed at a concentration of 10mg/ L (**Nataraj et al., 2007; Sadrzadeh et al., 2007; Li et al., 2021**).



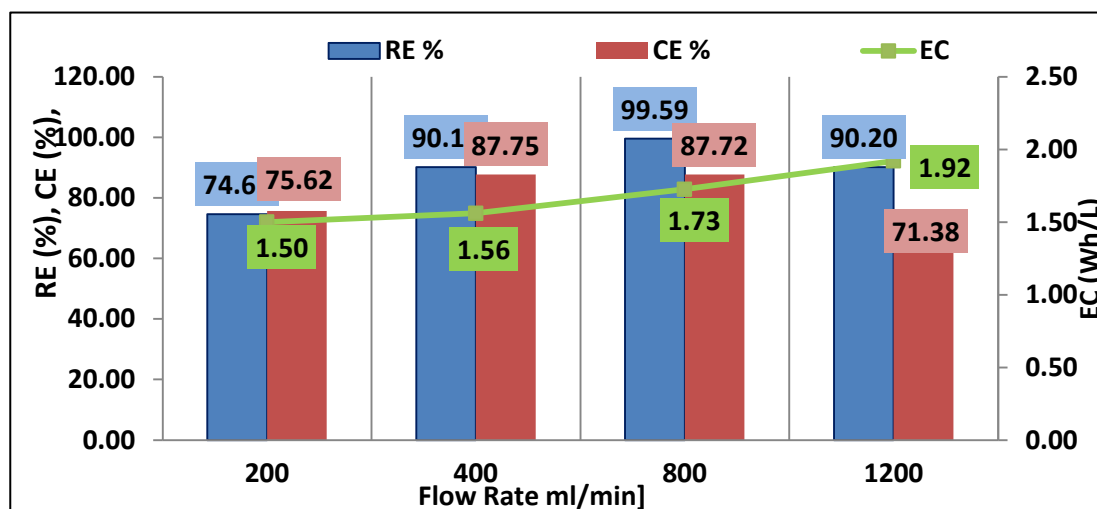
**Fig. 7.** (a) Effect of initial concentration on molar flux concentration ( $t= 60\text{min}$ ,  $Fr= 200 \text{ mL}/\text{min}$ , Voltage= 18V, pH 4 at T 25°C) and (b) Effect of Initial concentration on molar flux concentration with time ( $Fr= 800\text{mL}/\text{min}$ , Voltage= 18V, pH 4 at T 25°C).

Fig. (7a) shows the fluxes values of the copper removal of different concentrations solutions in the ED cell using an applied voltage of 18 V, pH 4 and flow rate 800 ml/min at 25°C. While, Fig. (7b) shows the flux values of different concentrations throughout successive periods of time. According to Fig. (7a), the flux clearly increased with the increase of initial concentration, which may be attributed to the excess of ions in the dilute solution and the increase of ions transfer to the electrodes, and hence the increase of flux values. It is worth mentioning that, there is a notable variation of the flux values between the low concentrations (10-100 mg/L) and the high concentration (200 – 400 mg/L), especially at the beginning of the process (Fig. 7b). However, with time, the rate of ions migration decreased sharply, and the flux values were close for all concentrations.

### The effect of flow rate

The flow rate is defined as the residence time of the solution in the compartment. As the flow rate increases, the retention time of the ions will decrease. The flow rate of the aqueous solution in the dilute and concentrate compartment is an important process parameter, which together with use of high voltages are responsible for occurrence of concentration polarization phenomena, and therefore can be controlled in order to limit it (Strathmann *et al.*, 2004). Consequently, it is known

that in ED processes, when the ions are moving towards the electrodes, their transport through the ion exchange membranes is faster than in the solutions. In the case of low flow rate, the retention time of the ions increases, and the formation of a concentration profile and the construction of boundary layers are observed near the membrane surfaces, and this concentration polarization phenomenon determines an increase in the resistance of the dilute due to the high resistance of the depleted boundary layer (Strathmann *et al.*, 2004; Tanaka *et al.*, 2007). The use of suitable flow rates during the batch ED can reduce the concentration polarization phenomenon by decreasing the thickness of the boundary layers at the membrane surfaces and thus can increase the transfer the ions through the ion exchange membranes.



**Fig. 8.** The effect of flow rate on RE, EC and CE ( $t= 60\text{min}$ ,  $C_i= 200\text{mg/L}$ , Voltage= 18V, pH= 4 at T 25°C).

The effect of flow rate (200, 400, 800 and 1200 ml/min) of dilute and concentrate solutions at 18V applied voltage, pH 4 for 200mg Cu/L was investigated. Data in Fig. (8) show that the increase in the flow rate from 200 to 800ml/ min enhanced the removal and current efficiency. This behavior is explained by the decrease in concentration polarization phenomenon via enhancing the hydrodynamics at the increase of the flow rate. Further increase of the flow rate from 800ml/ min to 1200 ml/min decreases the removal efficiency of  $\text{Cu}^{2+}$  from the dilute solution. This may be attributed to the absence of the effect of the increase of flow rate to 1200ml/ min on the concentration polarization and boundary layers. At the same time, the retention time of the ions was reduced, which has a reverse effect i.e. the liquid will arise as it does not undergo ion transfer between the membranes, and thus the removal and current efficiency decreases. As a result of the test, the flow rate of 800ml/ min is observed as the optimum value.

## CONCLUSION

In this work, the electro dialysis was shown to be effective for the removal of copper ions from synthetic wastewater. Initially, the electrode material and the distance between the electrodes and the membranes were determined for the unit design. There are not enough studies that dealt with the effect of electrode material and cathode/ anode distance. It is important to choose the suitable electrode material which is stable enough to treat heavy metal- contained solutions effectively. The fixing of the stainless-steel (SS 316) electrodes (anode and cathode) at a distance of 2 cm from the membranes was the best distance to increase the removal efficiency of heavy metals. Additionally, the effects of different parameters such as applied voltage, pH, flow rate, and initial concentration on removal efficiency, energy consumption, and current efficiency were investigated in this recirculated batch process, and the optimal operating conditions were determined. The applied voltage is the master parameter affecting the efficiency of the ED process in terms of high RE, high CE and low EC. The obtained data achieved that the applied voltage of 18 V is the appropriate voltage for the removal process in this designed ED. The pH has proven to be very effective in removing these ions and reducing energy consumption. The operation of the ED cell at an optimum pH value of 4 is more appropriate than operating at low or high pH values for the removal of copper (II) ions. The flow rate is an important parameter in the electro dialysis process. It can reduce the concentration polarization phenomenon due to the accumulation of substances in the membranes and increase the efficiency, but it can also negatively affect the removal efficiency by reducing the retention time in the membranes. As a result, the selection of an appropriate flow rate is critical. Therefore, the flow rate of 800ml/ min is observed as the optimum value. In the present study, the optimum values in terms of low energy consumption and high current efficiency for the removal of 200mg Cu/ L in 60min are 18 volts, pH 4, with a flow rate of 800 ml/min. There was a 99.59 % removal efficiency of Cu (II) with an energy consumption of 1.73 Wh/L and current efficiency of 87.72 %. One of the major advantages of this approach is the cost-effectiveness of the cell designed on a laboratory scale.

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