

Comparison of electro dialysis and reverse electro dialysis processes in the removal of Cu(II) from dilute solutions

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Abstract—Electrodialysis (ED) and electro dialysis reversal (EDR) processes have been often used for separation of ions in dilute solutions. In this study, the performance of ED and EDR processes has been examined in the removal of copper from the dilute solutions. First, applied voltage, initial concentration, flow rate, type of electrolyte and the effect of concentration were determined for both processes. Then, separation efficiency, current efficiency, energy requirement and material flux of the processes were calculated, and the performances of the processes were compared. The separation efficiency and energy consumption of EDR process were higher compared to ED process under equal operating conditions. Also, the current efficiency (39.58%) of EDR process was lower than the current efficiency (67.46%) of ED process. It can be said that the ED process is more suitable in terms of energy consumption for separation in the low flow rate and concentration.

Keywords: Electro dialysis, Electro dialysis Reversal, Cu (II) Removal, Process Performance

INTRODUCTION

Heavy metals in water environments show toxic and carcinogenic effects by entering the food chain [1,2]. Copper is a metal which is among these metals and which is toxic and also valuable. Copper may cause liver and sight impairments in humans as well as damaging the organisms in water environments. Such metals are required to be removed from waste waters both due to their environmental damages and legal obligations. Recovering the metal in waste waters for industrial process enables economic benefit and protection of natural resources. For this reason, the development of separation processes is very important for the separation of metal from dilute waste waters [3,4].

In case of production of clean water by recovering the metal from waste waters, it may be possible to operate as a closed system of industrial systems. Thus, economic contribution is provided by reducing the clean water and metal requirement of the industry. Moreover, the discharge of metal to the environment and the use of raw material sources becomes reduced [5,6]. Many studies have been performed for removing copper from waste water by using alternative treatment methods such as precipitation of the metal hydroxides, coagulation, adsorption, ion exchange, solvent extraction, electro dialysis, membrane technologies and reverse osmosis [7-10].

Electrochemical processes are deemed quite proper for removal or recovery of metals from diluted solutions due to their high separation efficiency, ability to recover metal and non-generation of sludge. For this reason, in the recent years, studies regarding the use and development of electrochemical separation methods are

increasing.

Electro dialysis is the basic process of electrochemical separation processes. ED process is the separation process in which the ion types in a solution move from one solution to another along ion exchange membranes under the effect of electric current. Nonformation of sludge in ED process is a significant advantage of the system. Electrochemical processes have different applications, which many of these are related to separation and reuse. In recent years, it is being used in obtaining drinking water, in removing salt from sea water, [11] in separating and concentrating acids [12], and in recovering metal salts from industrial wastewaters [13].

Electro dialysis cell couple consists of a concentrate section, a dilute section and two ion exchanger membranes. When electric current is applied to the cell, the cations passing through the cation exchange membrane move towards the cathode, and anions passing through the anion exchange membrane move towards the anode [14-17]. And thus, while the solution is losing its ions in one of the aligned sections, the solution in the section right beside it becomes concentrated. While the water obtained from the dilute section of ED process is able to be used again within the process, the water inside the concentrate section may be accumulated in a tank for recovering [18].

The limiting current density (LCD) is very important in the performance of electro dialysis process. By the decrease of ions within the treated solution, it approaches to LCD, in other words, the passage of current inside the system starts to become difficult, and when current is continued to be provided to the electrodes, there is formation of H⁺ ion and oxygen gas in the anode and the formation of OH⁻ ion and hydrogen gas in the cathode; furthermore, the temperature of water inside the reactor increases. For this reason, the ED process should be operated as close to LCD, but below it [13]. The removed ion amount depends on both the density of current and, area and number of the membranes. The

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formation of any fouling on the surface of membrane significantly affects the separation performance of ED process [19]. As it is worked at current values close to LCD, OH^- ion forms in the cathode section as the result of electrolysis reactions. This may cause the settlement of metal hydroxides on the surface of membrane and the formation of fouling. In the ED process, changing the direction of the electric current for 3-4 times an hour may decrease the formation of fouling. The processes designed in this manner are called electrodialysis reversal (EDR). During the short-term displacement of cathode and anode, the diluted and concentrated sections also displace. By this reverse current, the membrane may be cleaned by pushing the residue accumulating on the membrane inside the solution again [20-22]. Moreover, the formation of fouling may be decreased due to the effect of pulse realized on the surface of membrane [19]. For this reason, EDR process has started to be suggested instead of ED process in recent years.

In this study, ED and EDR processes were operated under the limiting current density for the prevention of any fouling on the membrane. The purpose of the study is to compare the separation efficiency, current efficiency, material flux and energy requirement values of ED and EDR processes being operated under equal operation conditions without having polarization of membrane. As the result of experimental studies, the effect of operation parameters such as the flow rate, initial concentration and applied voltage on each process was revealed.

1. Operation Parameters and Performance Indicators of ED/EDR Processes

As well as the operation principle of ED and EDR processes is essentially similar, their process performances may change under the effect of operation parameters such as the applied voltage, initial concentration, flow rate, type and concentration of electrolyte, change of pH, membrane characteristics, number of sections in ED cell and sequencing of membranes. The following performance indicators are used for the evaluation of the effect of operation parameters.

1-1. Determining of Limiting Current Density (LCD, mA/cm^2)

LCD can be determined by current measurement for both flow rate and concentration as a function of applied voltage. The current passing from unit area of membrane (current density) and applied voltage graph is drawn. The linearity of this curve starts to decrease when the applied voltage is up to a certain value. Reason for this is decrement of concentration in dilute solution and sharp

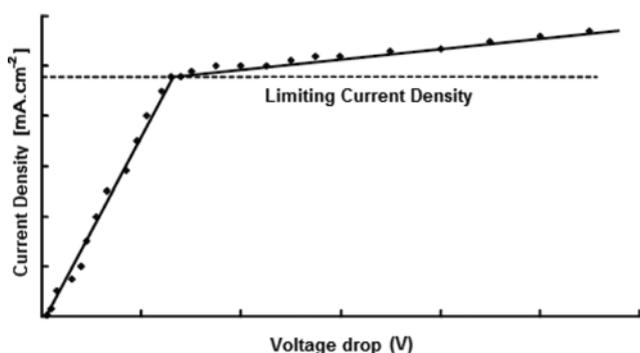


Fig. 1. Determination of limiting current density.

increment of resistance at the membrane boundary layer. Current density in this point of the curve is defined as the limiting current density (Fig. 1) [3].

1-2. Separation Efficiency (SP%)

The metal separation efficiency of ED process is the difference of metal concentration ($[\text{Cd}]_t$) in dilute section in the end of operation from initial metal concentration ($[\text{Cd}]_0$).

$$\%SP = \left(1 - \frac{[\text{Cd}]_t}{[\text{Cd}]_0}\right) \cdot 100 \quad (1)$$

1-3. Flux (J)

The amount of material ($V \cdot \Delta C$, mol) being carried from the effective membrane area (A , cm^2) at a specific time interval (t) is defined as the flux of the process (J , $\text{mol}/\text{cm}^2 \cdot \text{s}$). Here, V is the volume of concentrate section (L) and ΔC is the amount of material (mol/L) carried at time t [23,24].

$$J = \frac{V}{A} \cdot \frac{\Delta C}{t} \quad (2)$$

1-4. Current Efficiency (%CE)

During an operation time Δt (s), the ratio of ion amount (Δn , mol) being transferred from membranes in the process, to electric load (Q , Coulomb) passing from the system is current efficiency. So, current efficiency is the determination of current (I , A) used to carry one mol of ion at Δt time interval. The current efficiency being high indicates that the current (I) provided to the system is not lost in the system, that it is not carried by other ions or that it is not spent for the electrolysis of water.

$$CE = \frac{\Delta n \cdot z \cdot F}{N \cdot I \cdot \Delta t} \quad (3)$$

Here, F is the Faraday constant (96485 As/mol), and is the valence of ion. N specifies the stack number.

Energy requirement: the energy consumption required for the removal of ions at unit volume of the feed solution may be specified in the following equation [25,26].

$$EC = \frac{E \int_0^t I dt}{Vd} \quad (5)$$

EC is the energy consumption ($\text{Watt} \cdot \text{h}/\text{m}^3$), E is the applied potential (V), I is current (A), T is time (h) and Vd is the volume (m^3) of solution passing through the diluted section.

MATERIALS AND METHODS

All chemicals being used in experimental studies were of analytical purity. ED and EDR operations had been realized in Micro-FlowCell® electrodialysis cell with five sections of laboratory scale obtained commercially. ED cell included Pt/Ti electrodes as anode and cathode. The dimension of each of the electrodes was 90 mm × 46 mm, its thickness was 2 mm, and its effective area was 10 cm^2 . In the ED cell, the electric current was ensured by a direct current power source (Marxlow PS305-D). In the ED cell, Nafion117 was used as cation exchanger membrane, and Neosepta was used as anion exchanger membrane. Both membranes are resistant to acidic

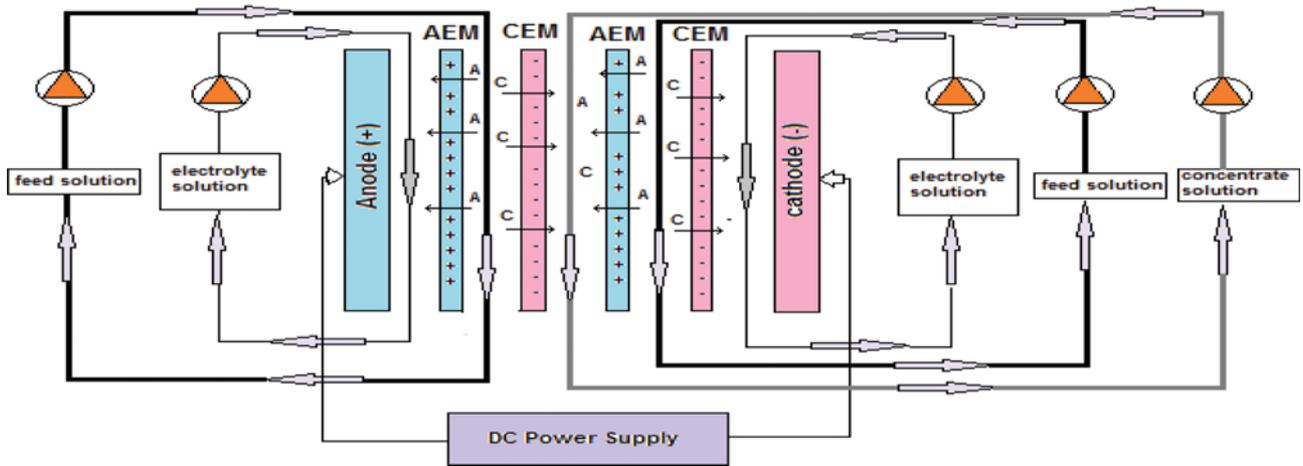


Fig. 2. Experimental set up.

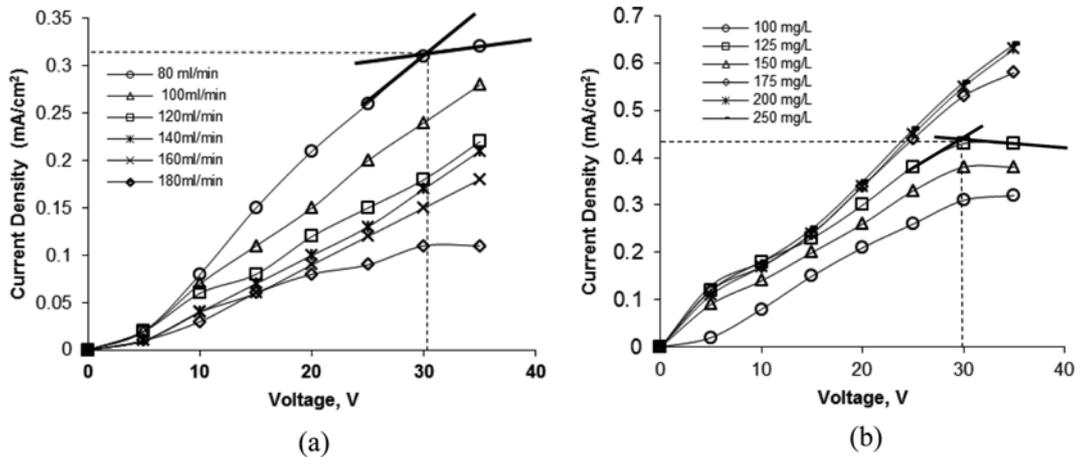


Fig. 3. Graph of current density and applied voltage (a) under different flow rates in ED process (b) when feeding solutions of different concentrations are used.

conditions. In the ED cell, each of the electrolytic solution, feeding solution and diluted solution were circulated to the process by using a peristaltic pump (ISMATEC MPC) from separate reservoirs of 1 L. To ensure the homogeneity of solutions, they were continuously mixed by electromagnetic mixer (DAIHAN MSH-20A). The studied experimental setup is presented in Fig. 2.

During the experimental studies, copper analysis was made in AAS (Atomic Adsorption Spectrometer) by periodically taking 1 mL samples from the dilute and concentrate compartments.

While experiments related to EDR process were being performed, the current being provided to the aforementioned ED cell was reversed two times an hour.

RESULTS AND DISCUSSION

1. Determination of the Limiting Current Density

For the ED process, tests were realized both at different flow rates (80, 100, 120, 140, 160, 180 mL/min) and at different beginning concentrations (100, 125, 150, 175, 200, 250 ppm). Maximum voltage for DC power supply used was 35 V. Therefore, the high-

est flow rate and concentration which be able to reach polarization curve in this voltage range was chosen for determining LCD. In the experiments, the current values passing from process were determined, when the voltage applied to the process was increased 5 volts in each 15 minutes (Fig. 3). The current density was calculated by using the area of membrane.

Linearity of curves in the graph drawn for the different flow rates only decreased for flow rate of 80 mL/min and 180 mL/min (Fig. 3(a)). In both linearity changed at applying voltage of 30 V. Corresponding current density value (LCD) to this potential was 0.31 mA/cm² for 80 mL/min. By the same way, when different initial concentration was used, LCD of 0.43 mA/cm² in voltage of 30 V was determined for initial concentration of 125 mg/L. Also, a study done by Lee [28] obtained similar LCD values. For comparison of processes, also in the EDR process current density found was 0.24 mA/s for flow rate of 80 mL/min and 0.63 mA/s for concentration of 125 mg/L. The current density of EDR was greater than that of ED (Fig. 4). To operate under the limiting current density is significant and required in order to minimize the energy consumption and polarization of concentration [23]. Moreover, it

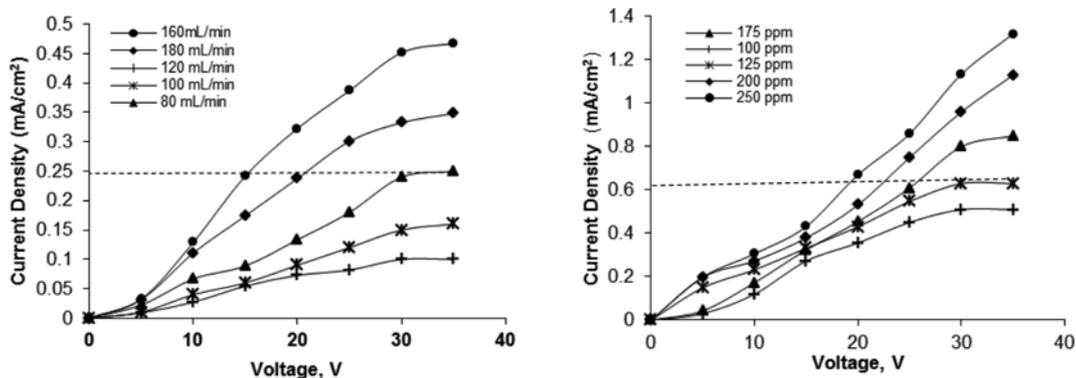


Fig. 4. Graphs of current density and applied voltage for both flow rate (a) and concentration (b) in the EDR process (it has been marked current density for flow rate and concentration correspond to LCD determined in the ED process).

is possible to obtain the best current efficiency at current values close to the LCD value [27]. When applied current over the LCD value or close, it may give rise to significant operation problems such as the blockage of membrane by the settlement of metal hydroxide and decrease of current efficiency due to the electrolysis of water. In the ED processes, working with about 80% of the LCD value is suitable for operating conditions to be efficient [27]. For this reason, 100%, 85% and 75% of 30 V were applied to the process in the following sections of the study.

2. The Effect of Applied Voltage

In the ED and EDR processes, experiments at different voltage values (30 V, 25, 5 V and 22, 5 V) were performed to be able to determine the effect of voltage on the processes. The feed solution concentration was 125 mg/L Cu²⁺. The current efficiency, separation efficiency and flux values determined for the processes applied different voltage values are provided in Fig. 5(a), and energy requirements are provided in Fig. 5(b).

As it will be observed from Fig. 4(a), the separation efficiency increased as the voltage applied to processes increased. At all voltage values, despite the current efficiency of EDR being low, separation efficiency, flux values were higher compared to ED, and it is partially more stable. In the EDR process, the lowness of current

efficiency may arise from the energy consumed during the reverse current being periodically applied in the process and from the re-passage of ions to dilute compartment within this period. In both processes, while the ion removal at high voltage is high, the energy used per mol ion is low. Despite the increase of energy consumption at low voltages, the removed ion amount had decreased. When low voltage is applied in the ED/EDR process, the decrease of ion transfer is possible as the overcoming the resistance of membranes becomes difficult [23]. In the EDR process, both the removed ion amount and used energy is higher than the ED process.

3. The Effect of Initial Concentration

Initial metal concentration is a significant parameter for defining the optimum operating conditions of the ED process [23]. In the ED and EDR processes, experiments were performed at different initial concentrations (100, 125, 175, 225, 300 mg/L) in order to be able to determine the effect of initial concentration. 30 volts of voltage and 80 mL/min flow rate had been applied to the processes. As seen in Fig. 6(a), the current efficiency reached to its highest level at 175 ppm (61, 21%) and then decreased in the EDR process. As for the ED process, the current efficiency decreased as the initial concentration increased. In the processes, the separation efficiencies are slightly decreasing when the initial concentra-

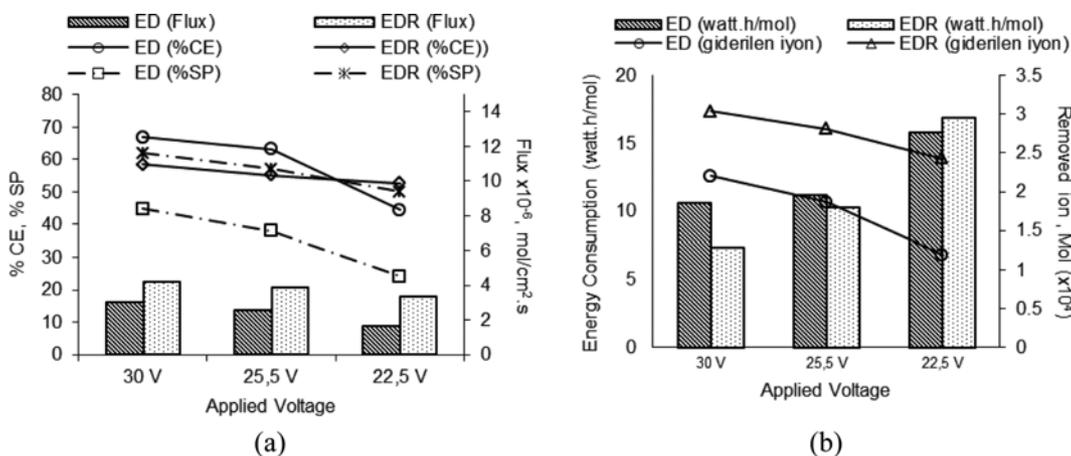


Fig. 5. At different voltages at ED and EDR processes, (a) flux, separation efficiency and current efficiency, (b) amount of consumed energy and removed ion (initial concentration 125 mg/L, flow rate 80 mL/min, working period 6 hours).

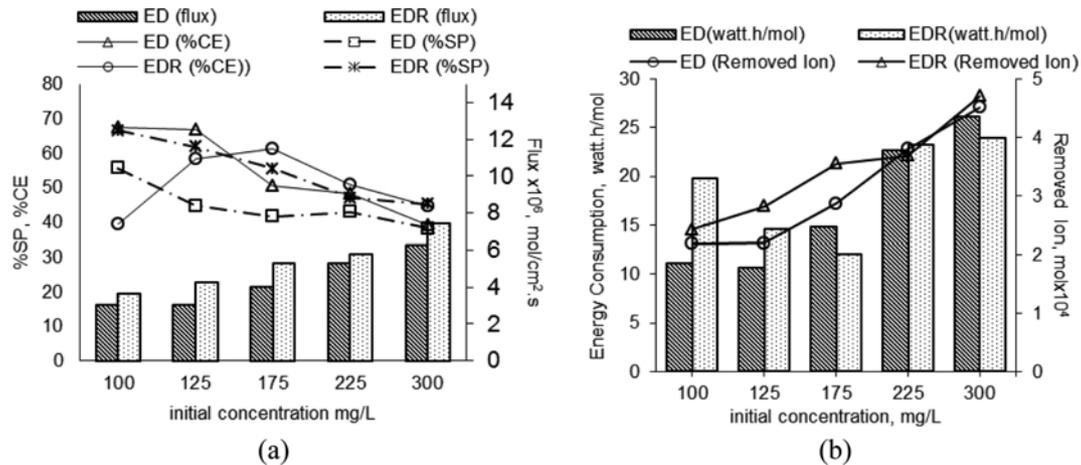


Fig. 6. At different initial concentrations at ED and EDR processes, (a) flux, separation efficiency and current efficiency, (b) amount of consumed energy and removed ion (applied voltage 30 V, flow rate 80 mL/min, operation time 6 hours).

tions increase. It is showing that the ion amount passing from the membrane is not increasing proportionally with the initial concentration. In fact, the ion amount being carried, in other words the flux, is slightly increasing by the increase of initial concentration. Separation efficiency (66.6% for EDR and 55.6% for ED) and flux (3.64×10^{-4} mol/cm²·s for EDR and 3.03×10^{-4} mol/cm²·s for ED) values of ED and EDR processes are quite close each other. By the increase of the ions in the EDR process, the current efficiency first increased, but then it decreased similarly to the ED process. In other words, the energy required for the transfer of ions had increased. The decrease of current efficiency and increase of the resistance of the system was possible due to lowness of voltage applied at high concentrations [24]. While energy usage was increasing in ED process by the increase of initial concentration [28], it first decreased and then increased in EDR process (Fig. 6(b)). When Figs. 6(a) and (b) are considered, the energy consumption is increasing while the current efficiency is decreasing. At high initial concentrations, in considered rate to removed ion amount the energy required by the EDR process is lower compared to the ED process. For this reason, it can be said that it is more economical at

higher concentrations.

4. The Effect of Flow Rate

In the ED and EDR processes, tests were performed at different flow rates (60, 80, 100, 130, 160, 200 mL/min) in order to be able to determine the effect of flow rate on the performance of processes. As increasing the flow rate will decrease the resistance of thin film layer on the surface of membrane, it may facilitate the passage of ions. As the time of remaining in the cell of the ions will decrease at higher flow rates, the rate of passage from the membrane also decreases, and the separation efficiency decreases [23,29].

The separation efficiency of EDR at low flow rates is higher compared to ED, but it is lower at high flow rates. In both ED and EDR processes, flux of material is slightly decreasing with the increase of flow rate. While the separation efficiency and current efficiency are decreasing along with the increase of flow rate in the ED process, energy consumption per mol is increasing. For the ED process, optimum flow rate was determined as 80 mL/min. In the EDR process, both the material flux and the energy used were high at low flow rates. Both were decreasing by the increase of flow rate. As seen, flow rate is effective for performance of both pro-

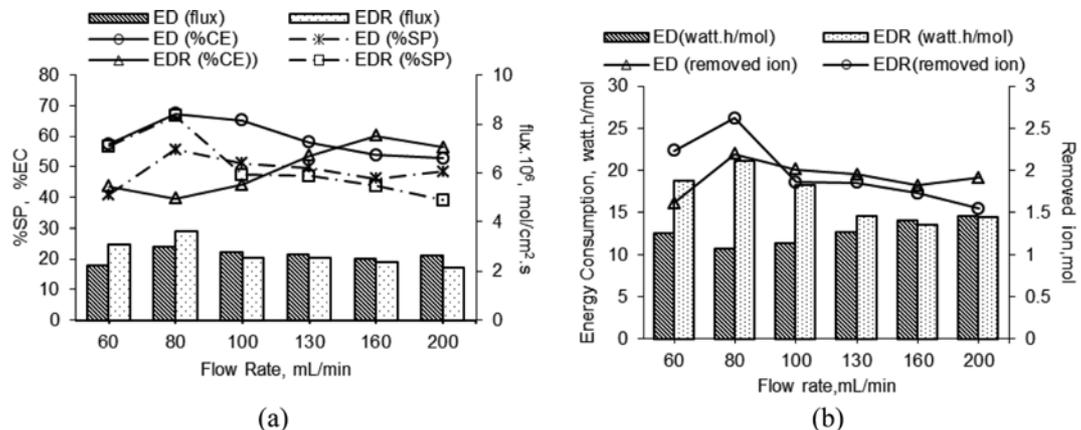


Fig. 7. For different flow rates at ED and EDR processes, (a) flux, separation efficiency and current efficiency, (b) amount of consumed energy and removed ion (applied voltage 30 V, initial concentration 100 mg/L electrolyte solution 0.3 M K₂SO₄, operation time 6 hours).

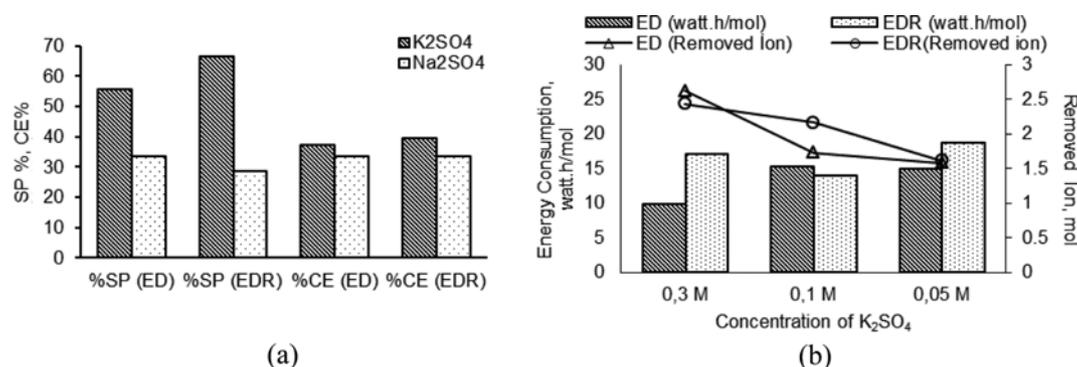


Fig. 8. In the ED and EDR processes, (a) The effect of electrolyte type on SP% and CE% values, (b) when different electrolyte concentrations are used, change of consumed energy and removed ion amount (applied voltage 30 V, initial concentration 100 mg/L, flow rate 80 mL/min, operation time 6 hours).

Table 1. Performance values obtained for the ED and EDR processes operated under the same conditions

Operating parameters		Performance values	ED	EDR
Applied voltage (V)	30	Separation efficiency (%)	55.69	66.63
Feeding concentration (mg/L)	100	Current efficiency (%)	67.46	39.58
Flow rate	80	Flux (mol/cm ² ·s)	3.03×10 ⁻⁶	3.64×10 ⁻⁶
Type and concentration of electrolyte	0.3 M K ₂ SO ₄	Consumed energy (watt·h/mol)	10.69	21.02

cesses. In considering flow rate (80 mL/min) optimum for both process, despite more energy requirement of EDR process its separation efficiency is better than ED.

5. The Effect of the Type and Concentration of Electrolyte

To determine the effects of type and concentration of electrolyte on the performance of processes, first the effect of the electrolyte type was examined by using 0.03 M K₂SO₄ and Na₂SO₄. Then, other experiments were performed using different concentrations of electrolyte (0.05 M, 0.1 M, 0.3M).

If ions in the electrolyte have high level of conductive value, this may have a positive effect on process performance. The electric conductivity value of K₂SO₄ is more than Na₂SO₄ at high concentrations [29]. For this reason, when K₂SO₄ was used as electrolyte, better separation efficiency was obtained both in the ED and EDR process. While difference among the ion removal efficiencies was significant, the current efficiencies were close to each other. In case of decrease of electrolyte concentration, while the ion amount removed was decreasing, the energy used was slightly increasing. As it approached to the precipitation limit of salts at higher concentrations, experiment was not performed for higher concentrations. Consequently, the use of electrolyte of suitable concentration and type is increasing the performance of both the ED and EDR processes. When the separation efficiencies are considered, it can be said that the characteristics of electrolyte solution have more effect on the performance of the ED process.

CONCLUSION

Within the scope of the study, ED and EDR processes were operated under the same operating conditions for the separation of copper ion from the dilute solutions. Thus, effects of all operation parameters on performance of each process have been revealed

as detailed. The results obtained for both processes operated under the optimum operating conditions which are determined for the ED process provided in Table 1.

When Table 1 is considered, the energy required for each mol ion separated in the process is about two-times more in the EDR process. The obtained separation efficiency and flux values are close to each other. It may be said that the ED process is more economic, for the case that the membranes have not yet had exposure to concentration polarization in the operating range. However, in the ED process, fouling that may arise in time in the membranes may also increase the energy requirement. According to the obtained experimental data, the optimum initial concentration of EDR (175 mg/L) is higher than ED (125 mg/L). The optimum flow rate values for both of processes are equal (80 mL/min); however, EDR has better flux value for the same flow rate. While the processes are providing good results at high electrolyte concentration, the separation efficiency of EDR is higher at the same electrolyte concentration.

ED/EDR processes can be design with efficiency of 50-90 percent [30]. But, maximum separation efficiency for the single step is approximately 70 percent [13]. Therefore, efficiency obtained for this study acceptable quite good.

In operation conditions suitable to LCD determined for ED process, current density of EDR is higher than that of ED process. Therefore, flux and separation efficiency for EDR is usually found higher. However, current efficiency is lower than ED at the same voltage. Along reverse current applying to EDR, some of ions return in to the dilute compartment from concentrate compartment and extra energy non-contributory for net ion transfer (flux) is used. Due to these, according to Eq. (4) and Eq. (5), current efficiency, that is the ratio between net ion transferred with energy used for all process may be lower than that of ED. Experiments in this

study is performed at ohmic location, result of this, polarization resistance is not just occurred. If there would studied in the polarization location, Current efficiency of EDR is may find bigger than that of ED.

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