

Influence of counter anions on metal separation and water transport in electro dialysis treating plating wastewater

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Abstract. Electrodialysis (ED) is used in wastewater treatment, during the processing and recovery of beneficial materials, to produce usable water. In this study, sulfate and chlorine ions, which are the anions majorly used for electroplating, were studied as factors affecting the recovery of copper, nickel and water from wastewater by electro dialysis. Although the removal rates of copper and nickel ions were slightly higher with the use of chlorine ions than of sulfate ions, the removal efficiencies were above 99.9% under all experimental conditions. The metal ions of the plating wastewater flowed through the ion exchange membrane of the diluate tank and the concentrate tank while all the water moved together due to electro-osmosis. The migration of water from the diluate tank to the concentrate tank was higher in the presence of a monovalent chloride ion compared to that of a divalent sulfate ion. When sulfate was the anion used, the recoveries of copper and nickel increased by about 25% and 30%, respectively, as compared to the chloride ion. Therefore, when divalent ions such as sulfate are present in the electro dialysis, it is possible to reduce the movement amount of water and highly concentrate the copper and nickel in the plating wastewater.

Keywords: electro dialysis; electroosmosis; metal separation; plating wastewater

1. Introduction

The plating wastewater is generated in the washing and rinsing process, which is located between the unit processes. (Dydo *et al.* 2018). Unit processes are several steps typically including alkaline and acid washing, plating and rinsing. The wastewater contains a variety of toxic substances such as washing agents, cyanides and heavy metals. The plating facility accounts for about 4% of the total wastewater discharges, and the plating wastewater constitutes 0.88% (48000 m³/d) of the total industrial wastewater (Min *et al.* 2019). The electroplating industry produces a large amount of heavy metal-containing wastewater, which can be treated to derive usable water and valuable metals. This would contribute toward transforming the existing structure of the consumption and disposal of resources into a resource-circulating one (Akretche *et al.* 2011). Furthermore, the gradual implementation of a water treatment system is necessary to prevent the excessive development of resources (Lee *et al.* 2018).

In general, many processes have been used to treat electroplating wastewater, such as adsorption, chemical precipitation, ion exchange, and electro dialysis (Fu and Wang, 2011, Ghorpade and Mansoor Ahammed, 2018, Kim *et al.* 2018). However, most of these processes have

problems, including the generation of sludge containing harmful contaminants, low recovery of valuable resources, large footprint and high operating cost (Min *et al.* 2019). Electro dialysis (ED) is one process that has many advantages such as short hydraulic residence time, small footprint, low sludge production, high recovery rate, and selective desalination (Feng *et al.* 2007).

The principle of ED is based on the selective transportation of cations and anions through ion exchange membranes (IEMs), under the influence of an applied voltage (Marti-Calatayud *et al.* 2012). An ED system consists of an alternating series of cation and anion exchange membranes (CEMs and AEMs), which are separated by spacer channels that allow for water flow along the membranes. In ED, an external voltage is applied between two end-electrodes to generate an ionic current through the membrane stack; therefore, the feed stream is desalinated and concentrated in alternating channels, and the concentrate and dilute are collected (Tedesco *et al.* 2017). The driving force for the ion transport in the ED procedure is the applied electrical potential between the anode and cathode. The applied electric field causes the migration of cations to the cathode and anions to the anode. During the migration process, anions pass through the anion exchange membranes, but are retained by the cation exchange membranes; a similar effect is seen with the cations.

Only an equal number of anion and cation charge equivalents are transferred from the diluate tank into the concentrate tank, and so the charge balance is maintained in each stream (Akretche *et al.* 2011). There are two reasons due to which water is transported across an ion exchange

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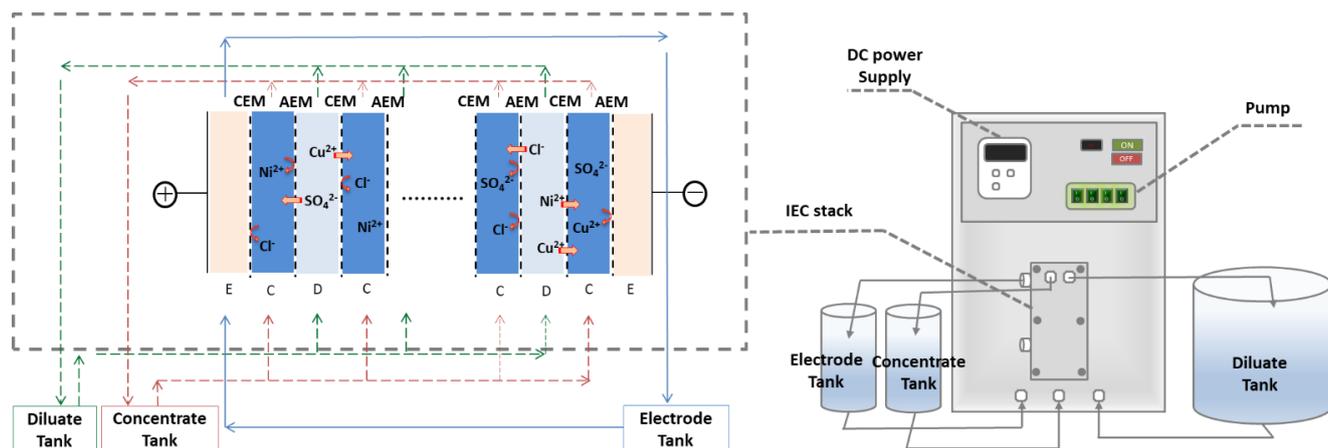


Fig. 1. Schematic diagram of the lab scale electro dialysis experimental set-up

membrane in ED: osmotic water transfer, due to concentration and osmotic pressure difference, and electroosmotic water transport, resulting from the migration of hydrated ions under the gradient of electrochemical potential. When the ions move from the diluate tank to the concentrate tank, the volumes of both the diluate and concentrate tanks change because of the electro-osmosis in which the hydrated water moves together (Jiang *et al.* 2015). Changes in the rate of water transfer can act as a major factor in ED because they can limit the concentrations of ions that could be concentrated. It has been hypothesized that to achieve equal exchange between monovalent anions and divalent cations in the ion exchange membrane, two molecules of ions migrate. Therefore, it was predicted that not only the rate of movement of monovalent anion but also the rate of movement of water would increase together.

In this work, the effect of counter anions in wastewater on the separation of heavy metals such as copper and nickel in ED process was investigated using chloride (Cl^-) and sulfate (SO_4^{2-}) possible anions in washing agents. This study was also performed to investigate the water transport properties during the migration of copper and nickel.

2. Materials and methods

2.1 Experimental setup

The electro dialysis process used in the experiment is shown in Fig. 1. Electro dialysis consists of a diluate tank, a concentrate tank, an electrode bath, an ion exchange membrane stack, a pump, an electrode, and a power supply. The volume of the diluate tank is 20 L, and that of the concentrate tank and the electrode solution tank is 0.5 L.

The power supply (P3030, Advantek, Bucheon, Korea) is capable of supplying voltage and constant current in the range of 0–300 V and 0–6 A, respectively. A 4% Na_2SO_4 solution was used as the electrode solution. The pump flow rate was 400 mL/min for the diluate tank, 700 mL/min for the concentrate tank, and 1,400 mL/min for the electrode solution tank. Electrical conductivity, pH, and current changes were recorded using a data storage device.

Table 1 Characteristics of the ion exchange membrane

Type	CSE	ASE
	Strong Acid (Na type)	Strong Base (Cl type)
Electric resistance ($\Omega \cdot \text{cm}^2$)	1.8	2.6
Burst strength (MPa)	≥ 0.35	≥ 0.35
Thickness (mm)	0.16	0.15
Temperature ($^\circ\text{C}$)	≤ 40	≤ 60
pH	0~14	0~14

Table 1 shows the performance of the ion exchange membranes used in the experiments. The ion exchange membranes used in this experiment were the NEOSEPTA® cation exchange membranes (CSE-SB) and the Astom anion exchange membranes (ASE-SB).

The effective area of each ion exchange membrane was 55 cm^2 . The thickness of the cation and anion exchange membranes were 0.16 mm and 0.15 mm, respectively, and the distance between them was 0.73 mm. The ion exchange membrane stack was composed of six cation and anion exchange membranes. The ion exchange membrane was thoroughly immersed in the target water for 24 h, and then pretreated by stirring.

2.2 Wastewater

Synthetic wastewater was prepared by plating wastewater containing copper and nickel, where Cl^- was used as a common anion, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were used as artificial wastewater, and where SO_4^{2-} was used as a common anion, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ were used as artificial wastewater. Electro dialysis experiments were carried out in batches. The volume of the solution was set at 20 L of diluate solution, 0.5 L of concentrate and electrode solution, with HCl and H_2SO_4 , respectively, used for pH adjustment.

2.3 Operation and analytical methods

An experiment was carried out in a constant voltage mode using a rectifier, by dividing the process between a diluate tank, a concentrate tank, and an electrode tank. The

initial concentration of copper and nickel was set at 20 mg/L for both the concentrate and diluate, to study the effect of water movement and current density during the electro dialysis of copper and nickel. The total operation time was 24 h. The copper and nickel concentrations were analyzed at regular intervals. A cylindrical water tank was used to measure and confirm the volume change of the concentrate and diluate tanks. The removal rate of copper and nickel in the wastewater in the electro dialysis experiment was calculated using equation (1), and the recovery was calculated using equation (2).

$$\text{Removal rate} = \frac{C_0 - C_t}{C_0} \cdot 100 \% \quad (1)$$

C_0 and C_t represent the concentration of copper and nickel before and after the electro dialysis operation, respectively.

$$\text{Recovery} = \frac{m_{cu}^{conct}}{m_{cu}^{dil_0}} \cdot 100 \% \quad (2)$$

The recovery rate was calculated by calculating the volume and concentration of each dilution and concentrate tank based on the amount of water movement. $m_{cu}^{dil_0}$ and m_{cu}^{conct} represent the mass of copper and nickel in the concentrate before and after the electro dialysis operation, respectively.

3. Results and discussion

3.1 Limiting current density

Limiting current density (LCD) was measured before proceeding with the experiment. In all electro dialysis experiments, the operating conditions are limited by the LCD. Beyond it, the concentration polarization worsens and the concentration of ions at the surface of the membrane in the dilution bath decreases drastically, necessitating the limitation of ion transport and high voltage, and resulting in economic losses (Martí-Calatayud *et al.* 2012). When the concentration of the solution is kept constant during the experiment and the applied current value is changed, the potential value changes linearly until the limit of the current value is reached. After this point, the slope changes abruptly, and the turning point is determined by the LCD (Kabay *et al.* 2006). Operation at the critical LCD minimizes the electrical resistance under the conditions of the membrane used, and the efficiency of the current is defined as the maximum current density that can be utilized (Yoon, *et al.* 2011). The experimental results for confirming the appropriate current density are shown in Fig. 2. The LCD values obtained were 0.99 mA/cm² for Cl⁻ and 1.41 mA/cm² for divalent ion SO₄²⁻, and the voltages for operating below the critical current density were 8.5 V and 10.1 V, respectively.

3.2 Removal of ions

The effect of the membrane separation process depends not only on the structural properties of the membrane

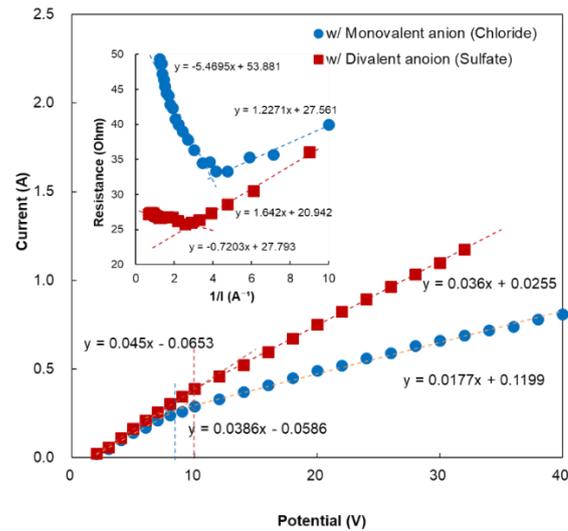


Fig. 2. Experimental and theoretical limiting current density (V-I curve)

Table 2 Ion radius and hydrated radius of the ions used

Ion	Ionic Weight (Da)	Ionic radius (nm)	Hydrated radius (nm)
Cl ⁻	35.5	0.167	0.324
SO ₄ ²⁻	96	0.215	0.3
Cu ²⁺	63.5	0.072	0.419
Ni ²⁺	58.7	0.069	0.404

but also on the size and electrical transport properties of the ions in the electrolyte. The amount of ion charge and the magnitude and intensity of hydration of the hydrated ion have a significant effect on the ions' ability to penetrate through the membrane (Ray 2008, Tansel 2012). Table 2 shows the ionic hydration radii of the anions present in the electro dialysis experiment for the recovery of copper and nickel from the plating wastewater and the processing of usable water.

Fig. 3 shows the concentration and removal rate of copper and nickel in the diluate tank. In transporting ions through cation and anion exchange membranes, multivalent cations interact more strongly with the membrane functional groups and are transported slower than monovalent ions. Additionally, the larger the ion, the more disturbed the movement of ions through the membrane (Van der Bruggen *et al.* 2004). Since Cl⁻ ions (0.167 nm) have a smaller ion radius than SO₄²⁻ (0.215 nm) ions, the removal rate of copper ions was faster when the anions were Cl⁻ (Fig. 3 (a)). Similarly, the removal of nickel occurred faster with monovalent ions (Fig. 3 (b)).

3.3 Recovery of metals

Since monovalent ions have a faster removal rate than divalent ions, the efficiency also increases more rapidly (Tansel 2012). The recovery of nickel proceeds in a similar manner. The concentration of copper and nickel ions in the concentrate was 365.7 and 380.1 mg/L, respectively, in the

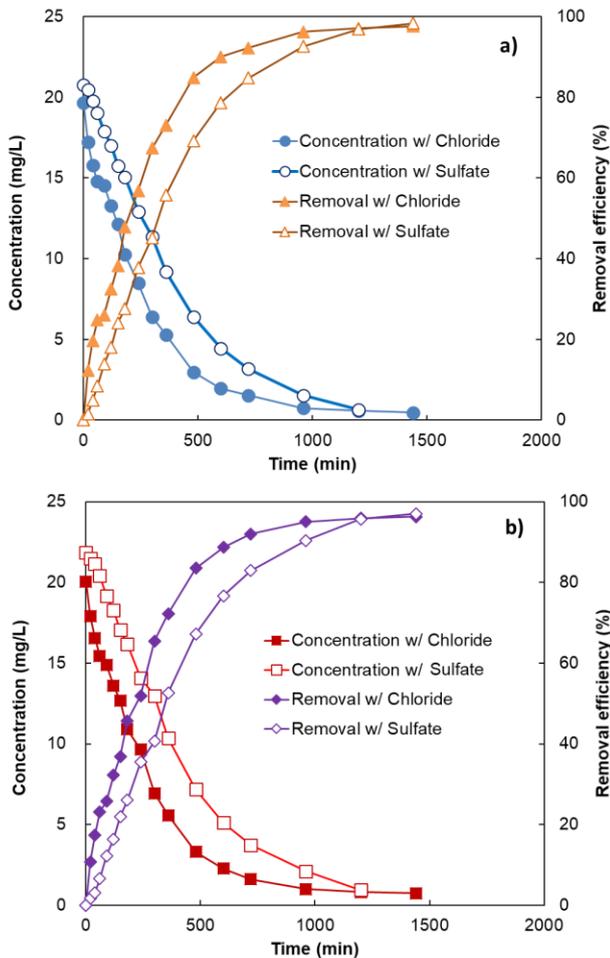


Fig. 3. The concentration and removal rate of (a) copper and (b) nickel during operation in diluate tank

presence of the Cl^- ion, and 546.6 and 600.6 mg/L, respectively, in the presence of the SO_4^{2-} ion.

The recovery can be calculated by taking into account the volume of water movement by electro-osmosis, as shown in Fig. 4. The recovery rate of copper based on the anions present was 66.24%, 92.64%, 67.46%, and 99.65%, respectively. The recovery rate of metals was higher with SO_4^{2-} ions than with Cl^- ions. This is presumably due to the decrease in the recovery of copper and nickel concentrates as well as the amount of treated water as the water moves from the diluate tank to the concentrate tank together by the electro-osmosis phenomenon.

3.4 Change of water movement

The selectivity of ion exchange membranes to ions is caused by three mechanisms: the size-based control of the selective permeability of ions with the same charge, the rejection of specific ions by a thin surface layer of a film having the same charge as the ions, and the specific interaction between the functional groups of the membrane and the moving ions (Sata *et al.* 1994). The anion selectivities of monovalent and divalent anions are reported in various articles (Kabay *et al.* 2006, Zhang *et al.* 2009), which can be attributed to the effect of ion size and charge.

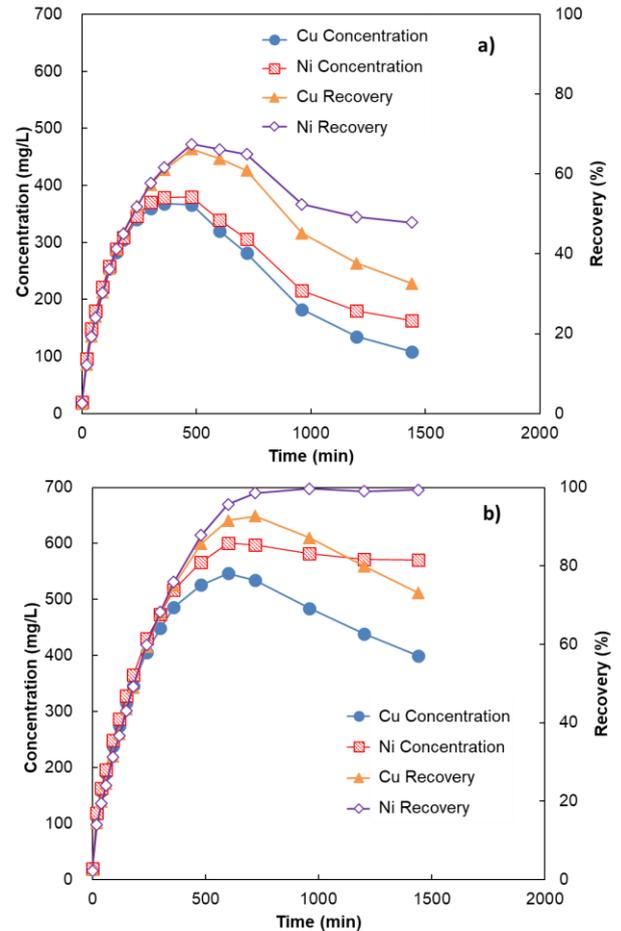


Fig. 4. Comparison of copper and nickel concentrations and recovery rates in the presence of (a) monovalent anions (Cl^-) and (b) divalent anions (SO_4^{2-}) during operation in a concentrate tank

Ions have their own physicochemical properties, such as ionic radius, hydration radius, and coordination number, which determine their migration through the membrane and affect the water transfer according to these differences. The smaller the atomic radius of the ion, the larger the sign radius and the greater the amount of water movement (Jiang *et al.* 2014, Jiang *et al.* 2015). Therefore, the volume change is shown in Fig. 5 to confirm the amount of water movement due to the electro-osmosis phenomenon in the electrodialysis experiment, taking ion radius and hydration radius into consideration. The migration of water due to electro-osmosis in the presence of the Cl^- ion increased due to the difference in the hydration radius between Cl^- (0.324 nm) and SO_4^{2-} (0.330 nm) (Table 2). Because an equal number of anionic and cationic charges are transferred in the ion exchange membrane, it is considered that two anion molecules migrate from the dilute cell to the enriched cell in the same manner as the monovalent anion and the divalent cation in order to maintain the charge balance (Akretche 2011). Therefore, when the copper ions and the nickel ions, which are monovalent anions, are treated as two-ionized ions, there is an increase in both the amount of water

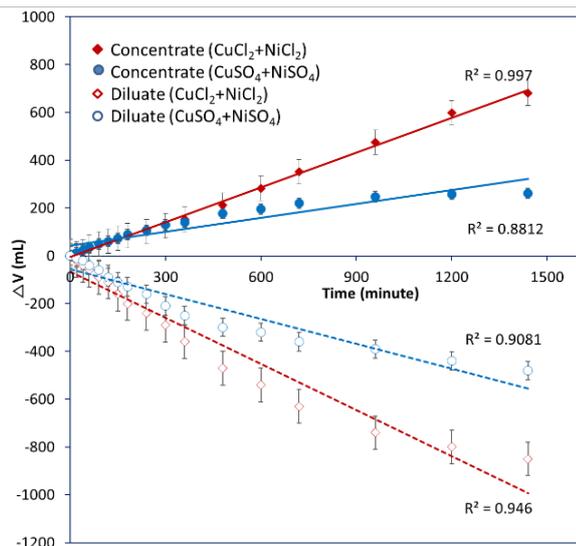


Fig. 5. Volume change of the diluate and concentrate tank

movement due to electro-osmosis, and the amount of water when the Cl^- ion is present and the concentration ratio is decreased.

5. Conclusions

The effects of SO_4^{2-} and Cl^- ions, the major anions present in the plating wastewater, on the recovery of copper, nickel, and usable water in the electro dialysis process have been studied. The monovalent anion (Cl^-) compared to the divalent anion (SO_4^{2-}) increased the rate of water transport. The migration of water accompanied by electro-osmosis also increased because the migration of Cl^- , which is a monovalent anion, doubled. In the concentrate tanks, the recovery rates of Cu^{2+} and Ni^{2+} , respectively, were 66.24 % and 67.46 %, in the presence of chlorine ions and 92.64 % and 99.65 % in the presence of sulfate ions. As the movement of the moving water increased, the concentrations of copper and nickel in the concentrate tank were higher when SO_4^{2-} was present than when Cl^- was present as the counterion. Based on the migration of the ions and water, we conclude that recovery of divalent heavy metal ions using SO_4^{2-} ions is advantageous. In order to improve the recovery rate of noble metals from plating wastewater, it is suggested that it is economical to use a chemical containing a multivalent anion as the salt used in the plating bath and the acid used in the cleaning.

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