Effect of anions on recovery of copper, nickel and water from electroplating wastewater in electrodialysis process

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ABSTRACT

Electrodialysis (ED) is one of the most promising ways for recovering copper and nickel from plating wastewater. The water moves together with the electroosmosis while the ions in the plating wastewater pass through the ion exchange membrane in the dilution tank and into the concentrated tank. Depending on the water transported from the dilution tank to the concentrating tank, there is a limit to the concentration of copper and nickel that can be concentrated with ED. In this study, it was confirmed that the migration phenomena of water and ions are affected by the difference of anions contained in plating wastewater. Since the charge balance of the ions is achieved, the charge of cations, such as copper and nickel which pass through the ion exchange membrane is the same as that of the ion anion. Therefore, the amount of migration of Cl⁻, which is a monovalent anion, is doubled compared with that of divalent ions, and the amount of migration of water accompanying electroosmosis also increases. When the anion was divalent SO₄²⁻, the concentration of copper and nickel ions in the concentration tank was higher than that of univalent Cl⁻.

Keywords: Electrodialysis, water transfer, plating wastewater

INTRODUCTION

In generally, many processes were used for treating plating waste water such as adsorption, chemical precipitation, ion exchange, electrodialysis and so on. Most processes have problems which have generating sludge contained harmful contaminants, low recovery of valuable resource, large footprint and high operating cost. As a remedy, electrodialysis (ED) can be used that has many advantages such as short residence time, small footprint, low sludge production, high recovery and selective separation. The principle of ED is based on the selective transport of cations and anions through ion exchange membranes (IEMs), under either the influence of an applied voltage. ED system consists of an alternating series of cation and anion exchange membranes, 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 at al., 2016). Only an equal number of anion and cation charge equivalent are transferred from the diluted tank into the concentrated tank and so the charge balance is maintained in each stream (Akretche at al., 2011). In the solution, the total amount of positive charges is the same as the total amount of negative charges and the concentration of cations and the concentration of anions present in the solution are the same based on charge balanced equation. The effect of the anions on the separation of divalent cations of copper and nickel
was investigated. When the ions move from the diluted tank to the concentrated tank, the volume of the diluted tank and the concentrated tank changes due to the electroosmosis in which the hydrated water moves together. Changes in the amount of water transfer can limit concentrations of can be concentrated ions, so they can act as a major factor in ED. In this paper, ED experiments were carried out in the presence of anions (Cl\(^{-}\), SO\(_4\)\(^{2-}\)) in order to investigate the effect of anions in solution on the separation of heavy metals such as copper and nickel in ED. The present study aimed to examine the migration behavior of copper, nickel and the water movement characteristics.

MATERIALS AND METHODS

Equipment and Analysis

The ED system (Neoregenbio, Korea) used in this study consisted of a diluted tank (inflow), a concentrated tank (effluent), an electrode tank, a pump (NH-3PX, Pan World, Ibarakiken, Japan), a DC power supply (EX 300-6 series, ODA, Korea), and a data collection system. A schematic diagram of the ED unit is shown in Fig. 1.

![Figure 1 Schematic diagram of lab scale electrodialysis experimental set-up.](image)

The ion exchange membrane stack has 5 cation exchange membranes (CSE, ASTOM, Japan), 5 anion exchange membranes (ASE, ASTOM, Japan), and an ion exchange membrane size of 0.55 cm\(^2\). The total effective membrane area was 5.5 cm\(^2\).

The amount of water transfer was measured the change in the height of the cylindrical tank. To determine the ion removal rate by ED, the concentrations of the concentrated tank and the diluted tank sampled over time were analyzed. The pH and the conductivity were recorded using the pH/EC meter (Orion Versa Star Pro, Thermo, USA) and the heavy metal ions were analyzed by inductively coupled plasma optical emission spectrometer (Thermo, ICP-6000 series, Japan).

Synthetic wastewater

Synthetic wastewater was prepared considering the concentration of plating wastewater contaminated by copper and nickel in industrial wastewater. In experiments using Cl\(^{-}\) as the anion, synthetic wastewater was prepared using CuCl\(_2\) \cdot 2H\(_2\)O and NiCl\(_2\) \cdot 6H\(_2\)O. In experiments using SO\(_4\)\(^{2-}\) as the anion, synthetic wastewater was prepared using CuSO\(_4\) \cdot 5H\(_2\)O and NiSO\(_4\) \cdot 6H\(_2\)O. ED experiments were carried out in batches. The volume of the solution was set at 0.5 L of diluted solution of 20 L of diluted solution and 0.5 L of electrode solution, and HCl and H\(_2\)SO\(_4\) were used for pH adjustment, respectively.
RESULTS AND DISCUSSION

Limiting current density

It is a limit current density of the important operating parameters from the ED. The current density is an important factor in calculating the required amount of membrane and operating cost for designing the process. Operation at high current densities without measuring the limiting current density will cause water degradation, resulting in increased energy consumption and irreversible damage to the membrane. In addition, an appropriate current density should be measured as it induces the formation of insoluble salt (Scale) by binding with heavy metal ions and OH⁻ ions generated by water decomposition. As a result of the limit current density experiment in the presence of Cl⁻ and SO₄²⁻ ions, the measured limit current density is 4.34, 7.83 mA / cm², respectively.

Water transport in ED

In general, water transport in the ED process refers mainly to osmosis and electro-osmosis. The former is caused by the difference in chemical potential between the diluted and concentrated compartments, a concentration gradient or osmotic-pressure difference, while the latter is caused by the migration of hydrated ions under an electric potential difference (Yan et al., 2019). The phenomenon in which water transfer through the ion exchange membrane limits the ion concentration that can be concentrated in the ED process. In other words, as ions and water transfer together, the concentration of the concentrated solution will have limits. Fig. 2 shows the variation of water transport for each anion.

![Figure 2 Water transport profile for different Anion as a function of time.](image)

Ion concentration variation

When Cl⁻ ions are present, more water is transported from the diluted tank to the concentrated tank. The difference in water transfer affects the concentration of copper and nickel ions in the concentrated tank. This will limit the amount of copper and nickel that can be recovered by concentration. Fig. 3 represents the concentration of copper and nickel in the concentrated tank of each ion. When Cl⁻ ions are present, the concentrations of copper and nickel ions in the concentrated tank are 365.7, 380.1 mg / L. When the SO₄²⁻ ion is present, the concentration of copper and nickel ions in the concentrated tank are 546.6, 600.6 mg / L.
Therefore, when Cl\(^{-}\) was present, it was found that the amount of water is increased, and the concentration of copper and nickel were decreased. When converted to mass in consideration of volume, When Cl\(^{-}\) ion is present, 0.291 g of copper and nickel 0.291 g. When SO\(_4^{2-}\) ions are present, the masses of copper and nickel are 0.385, 0.430 g, respectively, and there is a difference in the mass of copper and nickel that is maximally concentrated.

![Figure 3 The variation of Cu and Ni concentration in concentrate tank](image)

**CONCLUSION**

In this paper, investigated the effect of Cl\(^{-}\) and SO\(_4^{2-}\) ions on the separation of heavy metals such as copper and nickel in the ED process. As a result, the amount of water movement increased when monovalent anions (Cl\(^{-}\)) were present. According to the charge balance equation, anions having the same positive charge move when divalent cations of copper and nickel pass through the ion exchange membrane. Therefore, the movement amount of Cl\(^{-}\), which is a monovalent anion, is doubled, and the amount of movement of water accompanied by electroosmosis also increases. As the amount of water transfer increased, the concentrations of copper and nickel that could be maximally concentrated in the concentrated tank were higher in SO\(_4^{2-}\) than in the presence of Cl\(^{-}\).

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**REFERENCES**

