Membrane and Water Treatment, *Vol. 11, No. 3 (2020) 179-187*
DOI: https://doi.org/10.12989/mwt.2020.11.3.179

Electrodialysis of metal plating wastewater with neutralization pretreatment: Separation efficiency and organic removal

Yong-Min Park[1a], Su-Young Choi[1b], Ki-Young Park[1b] and Jihyang Kweon[*1b]

Department of Civil and Environmental Engineering, Konkuk University 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, Korea

(Received January 31, 2020, Revised February 25, 2020, Accepted March 4, 2020)

Abstract. Electrodialysis has been applied for treatment of industrial wastewater including metal electroplating. The wastewater from metal plating industries contains high concentrations of inorganics such as copper, nickel, and sodium. The ions in the feed were separated due to the electrical forces in the electrodialysis. The concentrate compartment is exposed to the elevated concentrations of the ions and yielded inorganic precipitations on the cation exchange membranes. The presence of organic matter in the metal plating wastewater affects complex interfacial reactions, which determines characteristics of inorganic scale fouling. The wastewater from a metal plating industry in practice was collected and the inorganic and organic compositions of the wastewater were analyzed. The performance of electrodialysis of the raw wastewater was evaluated and the effects of adjusting pH of the raw water were also measured. The integrated processes with neutralization and electrodialysis showed great removal of heavy metals sufficient to discharge to aquatic ecosystem. The organic matter in the raw water was also reduced by the neutralization, which might enhance removal performance and alleviate organic fouling in the integrated system.

Keywords: electrodialysis; metal plating wastewater; inorganic; organic; neutralization

1. Introduction

Metal electroplating wastewater contains numerous types of metals ions including harmful heavy metals and other toxic compounds such as nickel, chromium, copper, and cyanide. In order to protect ecosystems in natural streams and lakes from the exposures of these contaminants, electroplating wastewater should be treated before its discharge to the aquatic systems (Feng *et al.* 2019). Several treatment processes including precipitation, adsorption, ion-exchange, and reverse osmosis filtration, are employed to remove the harmful ions from the wastewater (Fu and Wang 2010). One of the conventional treatment process for the metal plating wastewater is the line-soda precipitation, which produces large volumes of sludge and sometimes provides insufficient removal efficiency for discharge to the aquatic environments. The adsorption has impeded by increases in adsorbent prices and ineffective reactivation of the exhausted adsorbent.

The advanced processes such as ion-exchange resin and membrane processes recently gain attentions for the high removal efficiency. Electro-dialysis (ED) is one of membrane process, in which ions in the feed are separated by ion-exchange membranes (IEMs) during ion transport due to the electrical forces. The ED has been used to treat industrial wastewater, brackish water, municipal wastewater, heavy metal removal and desalination (Choi *et al.* 2016, Park *et al.* 2017, Al-Amshawee *et al.* 2020). The advantages of ED include higher water recovery rates compared to reverse osmosis (RO), easy operation, long membrane lifetime, and capability to operate at high temperature. However, the higher cost of IEMs limited ED installation capacity compared to RO membrane. Huang *et al.* (2007) also indicated that fouling in IEMs restricted scaling up and applications of ED.

The ED shows high efficiency on separation of inorganics, which is essential for the success of the removal of the heavy metals. Selective removal of specific inorganics such as Mg^{2+}, Ca^{2+}, and Na^{+} has been achieved through use of selective IEMs (Choi *et al.* 2016). The ED is occasionally incorporated with electrolysis and electro-deionization for recovery of the heavy metals. The elevated concentrations of rejected ions in the retentate compartment are introduced to the electrolysis and the target ions are selectively precipitated and recovered. Membrane fouling occurs by particles, organic matter, inorganic ions, and growth of microorganisms depending on rejection rate of the specific membranes. For instance, low-pressure membranes such as microfiltration and ultrafiltration reject particles and some organic matter (Iritani *et al.* 2014, Zhang *et al.* 2014) but do not reject inorganics, therefore, particle fouling and some organic fouling occur and no inorganic precipitation appears. In ED, inorganic ions are transported through ion-exchange membranes and thus counter-ions are accumulated on the concentrate compartment. The rejected cations by anion-exchange membranes are the major inorganic foulants in ED. The fatty oils and surfactant are also included in the electroplating wastewater. Those are common additives to increase anti-corrosive properties of metal-coated products. Lafi *et al.* (2019) mentioned the

---

[*] Corresponding author, Ph.D. Professor
E-mail: jhkweon@konkuk.ac.kr
[a] M.S. Student
[b] Ph.D.

ISSN: 2005-8624 (Print), 2092-7037 (Online)

Table 1 Key water qualities of the raw and neutralized wastewater

	pH (-)	Conductivity (mS/cm)	Cu^{2+} (mg/L)	Ni^{2+} (mg/L)	Zn^{2+} (mg/L)	DOC (mg/L)
Raw	1.7	18.4	419.0	185.4	21.6	153.0
Neutralized	6.0	10.0	27.5	73.8	6.6	78.8

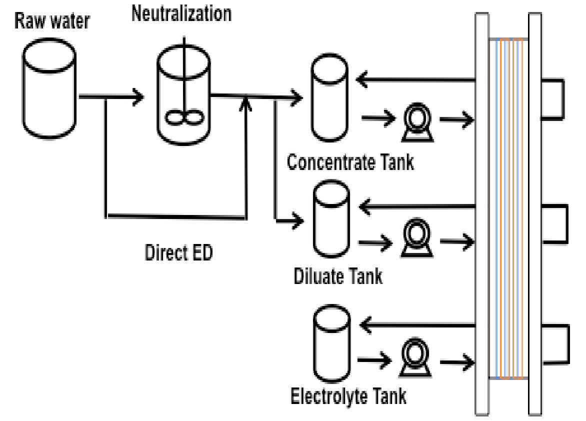

Fig. 1 Schematic diagram of neutralization and ED processes in this study

importance of interaction of inorganic and organic matter. In the study, a cationic dye solution showed fouling due to electrostatic interaction between cations of dyes and the fixed charges in the ion-exchange membrane and affinity interactions. Woźniak *et al*. (2014) suggested the removal of heavy metals and organic matters prior to ED due to the fouling on the IEMs surface. The precipitation was considered as a pretreatment of ED for the removal of inorganics and organic matter, which might yield fouling during the ED operation. The neutral pH was used to avoid production of massive sludge. During the precipitation, organic matter could play roles for the crystallization processes of inorganics. In this study, a wastewater from the metal plating industry was collected and the performance of ED for the removal of heavy metals was evaluated using the raw wastewater and the treated water by NaOH precipitation. In addition, composition of the organic matter in the metal plating wastewater was analyzed to understand its effects on the precipitation and on the fouling in the concentrate compartment.

2. Methods and materials

2.1 A metal plating wastewater

The wastewater treatment plant for the metal plating industries is located at the city of Namyangju (Gyunggi, Korea). About 40 L of the wastewater was collected in March, transferred to the laboratory, and stored at the refrigerator before use. The NaOH with a concentration of 1 M was used to neutralize the wastewater. The water qualities were analyzed and summarized in Table 1. The pH of the raw water was substantially acidic and the conductivity was also very high. The neutralization showed a higher removal of Cu with approximately 93%, compared to the 60% removal of Ni and 69% removal of Zn. The conductivity was reduced only 46% by neutralization, which indicated that there were many other metal ions with less removal rates than the above three metal ions. The dissolved organic carbon (DOC) of the raw water was 153.0 mg/L and the DOC concentration was reduced 48.5% by neutralization.

2.2 Electrodialysis

An ED system (CJ-S3, Changjo Techno Co. Ltd., Korea) was installed at the laboratory. The system was consisted of a diluate solution tank, a concentrate solution tank, an electrolyte solution tank, an ion-exchange membrane stack, and pumps. The ED cell was packed with five pairs of ion exchange membranes (cation and anion) and a pair of platinum plated titanium electrodes (anode and cathode). The ion exchange membranes were the NEOSEPTA® series membranes (ASTOM Co. Ltd., Japan). The cation exchange membrane was CMX-SB and anion exchange was AMX-SB. The surface area of each ion exchange membrane was 13.75 cm^2, and the total ion exchange membrane area of the stack of five membrane pairs was 275 cm^2. A schematic diagram of the experimental setup is shown in Figure 1. The limiting current was measured by increasing voltage stepwise. The volts started at 1 volt and increased to 30 volts for the raw water and to 50 volts for the neutralized water. The current measurement was conducted for five minutes at each voltage. The limiting current was occurred at the voltage of 8 with a value of 21.6 mA/cm^2 for the raw water and that of 46 with a value of 60.0 mA/cm^2 for the neutralized water. The ED performance was compared at the applied voltage of 8 using the raw and the neutralized waters. The effects of applied voltages were evaluated at the voltage of 8V and 30V with the neutralized water.

2.3 Analytical methods

The metal concentrations in the diluate and concentrate solutions were analyzed to evaluate their separation efficiency by electrodialysis. All samples were filtered with a 0.45 μm syringe filter to remove suspended solids. Copper and nickel were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES, ICP-6000, Thermo Fisher Scientific Inc., U.S.A.). The electrical conductivity and pH of the solution were measured using an Orion 5 Star instrument (Thermo Fisher Scientific Inc., U.S.A.). To observe chemical properties of organic compositions of the raw water and the neutralized water, the Fourier-transform infrared spectroscopy (FT-IR, Thermoscientific, U.S.A.) was employed. To analyse the infrared spectrum, each 50 mL of the sample water was

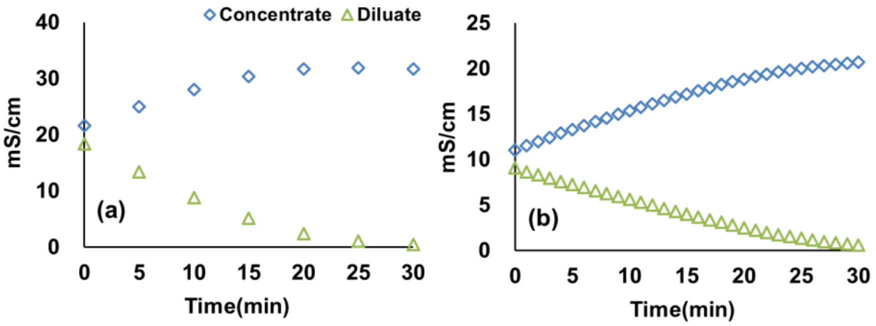

Fig. 2. Changes of conductivity during ED at 8 volts. (a) the raw water, (b) the neutralized water

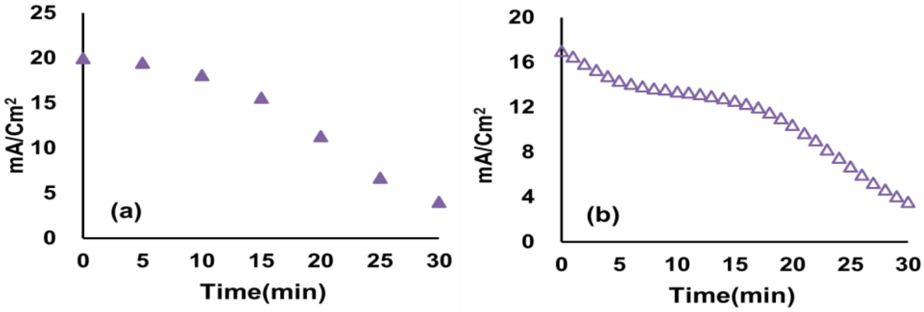

Fig. 3. Changes of current density during ED at 8 volts. (a) the raw water, (b) the neutralized water

Table 2 Ion concentrations and removal rates in diluate compartment of the ED operation with the raw water

Time (min)	Cu (mg/L)	Ni (mg/L)	Cr (mg/L)	Zn (mg/L)
0	419.0 (-)	185.4 (-)	16.3 (-)	21.6 (-)
5	222.7 (62.6%)	99.4 (62.5%)	11.4 (38.9%)	12.1 (60.2%)
10	156.9 (74.9%)	69.7 (75.0%)	10.0 (44.7%)	8.6 (72.5%)
15	105.2 (84.9%)	46.4 (85.0%)	9.0 (52.3%)	3.9 (82.3%)
20	63.2 (91.9%)	27.7 (92.3%)	7.8 (61.1%)	3.8 (89.7%)
25	34.1 (96.1%)	14.2 (96.6%)	6.4 (67.0%)	2.2 (93.4%)
30	16.6 (98.1%)	6.3 (98.6%)	5.0 (75.0%)	1.4 (95.6%)
Effluent standard for discharge	**1.0**	**0.1**	**0.5**	**1.0**

Table 3 Ion concentrations and removal rates in diluate compartment of the ED operation with the neutralized water

Time (min)	Cu (mg/L)	Ni (mg/L)	Cr (mg/L)	Zn (mg/L)
0	24.3 (-)	77.0 (-)	0.025 (-)	5.8 (-)
5	15.4 (36.6%)	51.6 (33.0%)	0.025 (-)	3.9 (32.9%)
10	. 103 (57.6%)	36.3 (52.8%)	0.025 (-)	2.7 (52.9%)
15	6.5 (73.3%)	24.2 (68.5%)	0.025 (-)	1.8 (68.2%)
20	3.9 (83.9%)	14.9 (80.6%)	0.015 (40.0%	1.0 (82.0%)
25	2.4 (90.0%)	8.675 (88.7%)	0.015 (40.0%)	0.6 (90.0%)
30	1.6 (93.4%)	4.7 (93.8%)	0.005 (80.0%)	0.3 (95.2%)
Effluent standard for discharge	**1.0**	**0.1**	**0.5**	**1.0**

dried using a freeze dryer (Ilshin Lab co., Ltd. Korea) for 24 hours at a vacuum pressure of less than 50 mTorr at -40'C. The dried powder was mixed with the KBr (potassium bromide, Sigma Aldrich) at a ratio of 1:100, for which 0.1 g of KBr was mixed with 0.001g of sample water. The mixed specimen was then compressed and scanned using the FT-IR (Thermoscientific, U.S.A.) devices.

The powder of humic acid (Sigma Aldrich, U.S.A.) and sodium alginate (Sigma Aldrich, U.S.A.) from the bottle was directly used to be mixed with KBr without the freeze drying procedure. Another technique, i.e., the fluorescence excitation-emission matrix (F-EEM) was used as an analytical method for qualitative analysis of organic matter. The water samples were filtered with 0.45μm syringe filter, placed in a 1-mL volume of the quartz cell, then the EEM spectra was scanned by a spectroscopy (RF-5301, Spectrofluorometer, Shidmazu, Japan). The samples were diluted with distilled water so that they did not exceed a fluorescence intensity of 1,000 arbitrary unit (a.u.). The excitation (Ex) wavelengths of 220 nm to 400 nm were scanned and the emission (Em) wavelengths of 280 nm to 600 nm were scanned. The measured intensities were visualized by creating a 3-D Contour plot using MATLAB 7.8 (Mathworks, Natick, MA, U.S.A.).

3. Result

3.1 Conductivity and current density

The conductivity changes during ED were evaluated to understand ion separation efficiency. The potentiostatic voltage mode was used to maintain 80% of the limiting current density. The applied voltage was 8 volts for the raw and the neutralized water. In addition, the constant voltage mode is safer than a constant current because a galvanostatic mode with constant current could produce occasionally high voltages across the membrane when small amounts of ions are remained in the diluate compartment (Gherasim, *et al.* 2014). The conductivity of the raw water became constant after approximately 25 minutes of operation was conducted and the infinitesimal reduction was occurred later on as shown in Figure 2. The conductivity of the raw was 18.4 mS/cm and that was decreased to 0.5 mS/cm after the 30 minutes of the operation. The reduction rate of the conductivity was 97.3%. As shown in Table 1, the neutralization removed approximately 46% of the conductivity, thus the initial conductivity of the treated water was 10.0 mS/cm and it was reduced steadily to 0.7 mS/cm during 30 min of the ED operation.

The reduction rate was 93%. However, the current density was decreased gradually as shown in Figure 3. The applied voltage is a critical factor for the ED operation because the voltage determines the current in the ED, which affects the separation efficiency of metals and also energy consumption (Banasiak *et al.* 2007, Walker *et al.* 2014, Scarazzat *et al.* 2015).

The ion separation exerted by conductivity reduction might change the pH of diluates and concentrates. The pH of the raw water was 1.7 and that of that of the neutralized water was 6.0 as shown in Table 1. During the ED, the pH was measured at every five minutes. The pH of diluate was increased gradually and the pH of the concentrate was decreased slowly, regardless of feed water. The rate of change was more rapid in the diluate part. The study by Walker *et al.* (2014) showed the same pattern such that the increase in pH of the diluate and the decrease in pH of the concentrate. The authors noted that the causes of pH variations included concentration polarization in the boundary layer, water dissociation, transferring of weak acid through anionic exchange membranes, membrane selectivity, and diffusivities differences of cations and anions.

3.2 Separation efficiency of heavy metals during ED

The electroplating wastewater contains various hazardous metal ions including Cu, Ni, Cr, and Zn. The separation efficiencies of those metal ions in the raw wastewater are summarized in Table 2 and Figure 4. The Cu concentration was the highest, i.e., 419 mg/L among the other metal ions. Copper coatings are used for corrosion protection and for producing smooth and uniform coverage by reacting other metal ions. For instance, the less reactive copper coating protects the more reactive iron from attack by acidic reagents. Nickel, chrome and zinc are also used to make decorative or non-corrosive metal surfaces. Chrome plating is sometimes applied to make surface for easy cleaning or surface hardness. The reduction rates of the metal ions in the diluate were ranged in between 75.0%~98.6% with the 30 minutes of ED operation of the raw water. The removal rate was 98.6% for Ni, 98.1% for Cu, 95.6% for Zn, and 75.0% for Cr. However, all the in concentrations in diluate compartment was not able to satisfy the effluent standard for discharge in Korea with 30 minutes of operation.

The removal rates of the metal ions in the neutralized water are presented in Table 3 and Figure 5. The neutralized water contained greatly low amounts of ions such that the initial concentrations were 24.3 mg/L for Cu, 77.0 mg/L for Ni, 0.025 mg/L for Cr, and 5.8 mg/L for Zn. The Cr concentration after the neutralization already met effluent standard of discharge in Korea, which indicating that the neutralization process was very effective to remove chromium ions from the wastewater. The reduction rates with 30 minutes of ED operation were 93.4% for Cu, 93.8% for Ni, and 95.2% for Zn. The Zn was effectively removed by ED such that only about 20 minutes of ED operation was enough to satisfy the effluent standard for Zn discharge. However, the Cu and Ni ions were difficult to lower the concentration below the effluent standard with these operating conditions. The Cr separation in ED was relatively slow compared to Cu, Zn, and Ni for the raw and the neutralized waters. The separation of ions is achieved by transport of the ions through membranes. Van der Bruggen *et al.* (2004) noted that the characteristics of the ion exchange membranes explained the slow transport of multivalent ions. The cationic exchange resin of the

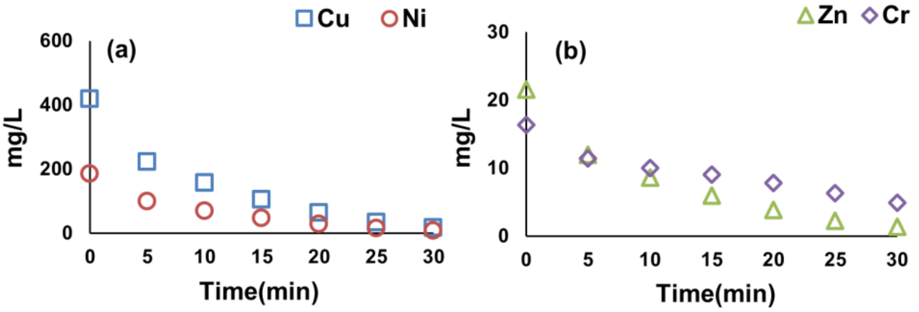

Fig. 4. Removal of metal ions during ED operation for the raw water. (a) Cu and Ni, (b) Zn and Cr

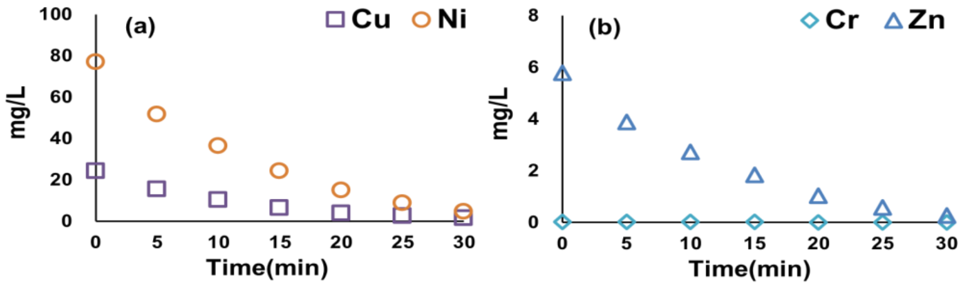

Fig. 5. Removal of metal ions during ED operation for the neutralized water. (a) Cu and Ni, (b) Zn and Cr

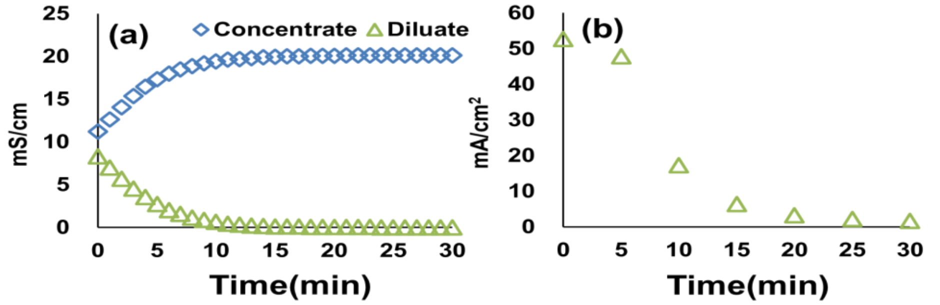

Fig. 6. ED performance at 30 volts with the neutralized water. (a) conductivity and (b) current density

Table 4 Ion concentrations and removal rates in diluate compartment of the ED operation with the neutralized water at 30 volts

Time (min)	Cu (mg/L)	Ni (mg/L)	Cr (mg/L)	Zn (mg/L)
0	30.6 (-)	70.5 (-)	0.19 (-)	7.5 (-)
5	13.76 (55.0%)	23.46 (66.7%)	0.07 (65.8%)	2.9 (61.7%)
10	3.91 (87.2%)	3.7 (94.8%)	0.07 (63.2%)	0.9 (87.4%)
15	1.09 (96.4%)	0.895 (98.7%)	0.04 (78.9%)	0.5 (92.8%)
20	0.65 (97.9%)	0.675 (99.0%)	0.03 (84.2%)	0.5 (93.2%)
25	0.51 (98.3%)	0.565 (99.2%)	0.03 (86.8%)	0.5 (93.0%)
30	0.66 (97.8%)	0.62 (99.1%)	Not available	0.7 (91.1%)
Effluent standard for discharge	1.0	0.1	0.5	1.0

membrane strongly retained the higher charged ions than the monovalent ions which yielded the slow transport rate through the cation exchange membrane. It should be note that the majority of chromium in the raw water taken from the wastewater plant in this study was a hexavalent form of chromium. Marti-Calatayud *et al*. (2018) also emphasized that diverse phenomena might arise during transport of multivalent ions through cationic exchange membranes under severe concentration polarization conditions and membrane selectivity and current efficiency in the electro-membrane processes might be influenced by the speciation and the form of complex species of multivalent ions.

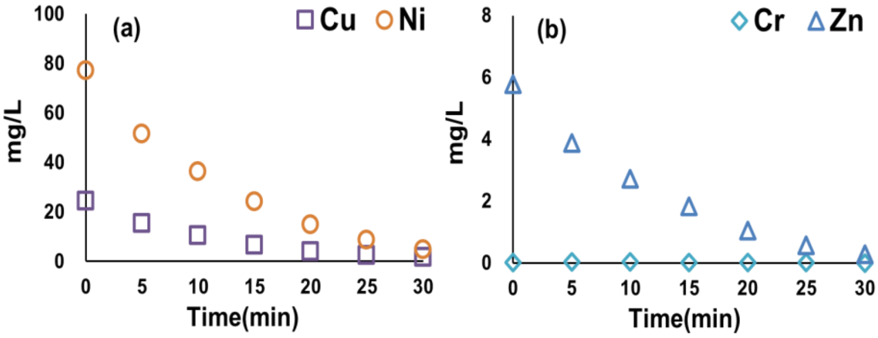

Fig. 7 Removal of metal ions during ED operation for the neutralized water at 30 volts. (a) Cu and Ni and (b) Zn and Cr

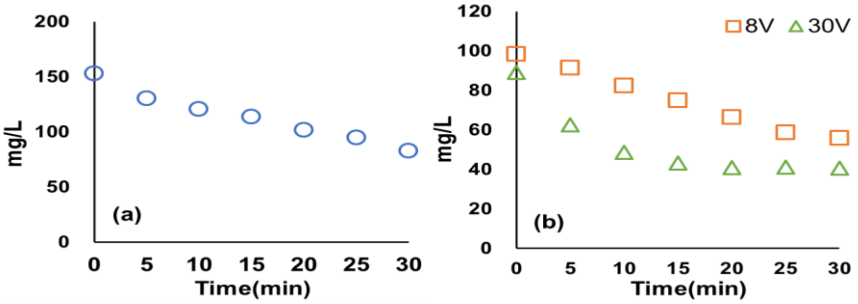

Fig. 8 Reduction of DOC during ED. (a) the raw water and (b) the neutralized water.

Table 5 Variations in DOC concentrations during ED

Time(min)	0	5	10	15	20	25	30
Raw water	153.0	130.3 (14.8%)	120.7 (21.1%)	114.0 (25.5%)	101.9 (33.4%)	95.0 (37.9%)	82.9 (45.8%)
Neutralized water (8V)	98.5	91.5 (7.1%)	82.3 (16.4%)	74.8 (24.0%)	66.3 (32.7%)	58.8 (43.3%)	55.8 (43.3%)
Neutralized water (30V)	89.0	62.5 (29.8%)	48.8 (45.2%)	43.4 (51.3%)	40.9 (54.1%)	41.2 (53.7%)	40.8 (54.2%)

3.3 Effects of applied voltages on ED operation with the neutralized water

The applied voltage was increased to understand its effects on the ED performance and to improve ion separation rate for satisfaction of the effluent standard of discharge in Korea. The applied voltage determines the current in the ED, which affects the separation efficiency of metals and also energy consumption (Walker *et al.* 2014, Scarazzat *et al.* 2015). Fig. 6 shows the changes in conductivity and current density at the 30 volts. The conductivity change was substantial and it was reduced to 0.9 mS/cm after just 10 minutes of ED operation. The reduction rate was 89.5%. However, the current density was decreased substantially corresponded to the decreases in the conductivity. The removal rate with the neutralized water at the 30 volts of the applied voltage was summarized in Table 4. The removal was greater compared to the results from the applied voltage of 8 volts. The removal of Cu and Zn was great and could meet the standard with 20 min and 10 min of ED operation, respectively, which indicating that the short operation time was required due to the high applied voltage. However, the Ni concentration at the diluate could not achieve the concentration below the standard even with the high voltage of 30 volts.

3.4 Removal of organic matter in ED

Although a majority of the metal plating wastewater was inorganic ions, some organic matter were also present in the wastewater due to the fatty acid and surfactants, which were added to increase resistances to corrosion of the coated surfaces (Feng *et al.* 2019). The DOC concentration of the raw water was 153.0 mg/L. The reduction of organic matter occurred steadily and 45.8% of the organic matter was removed with 30 minutes of ED operation. The neutralization reduced approximately 36–42% of organic matter of the raw water, so the initial DOC concentration in the neutralized water was 89.0–98.5 mg/L. The reduction of DOC with the neutralized water was increased with increasing operating time. The final DOC concentrations of the diluate were 55.8 mg/L at 8V and 40.8 mg/L at 30V. The DOC removal rate by ED was ranged in 43.3–54.2% for the neutralized water. The removal pattern of organic matter was corresponded with the increases in the voltage. The removal of inorganic ions were directly related with the applied voltage since the driving force of separation was electrical potential. Similarly, the removal of organic matter might be also governed by the transport by the electrical force. In addition, the reduction of the DOC concentration was gradual with 8 V of operation and it was substantial at the relatively early time of ED operation with 30 V of

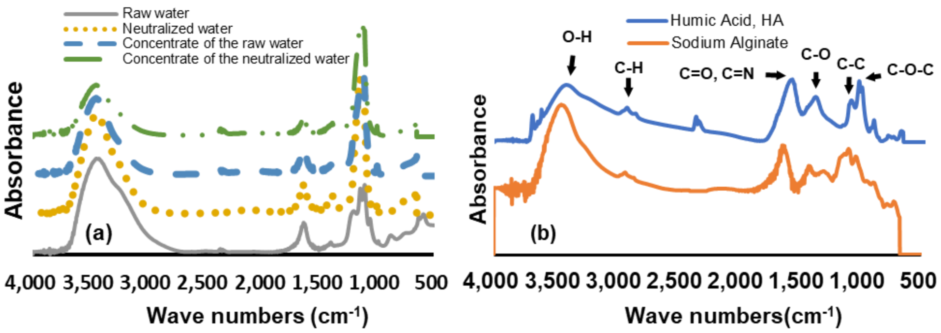

Fig. 9 The FTIR spectra of (a) feeds and concentrates of the raw and neutralized waters (b) the model organic compounds

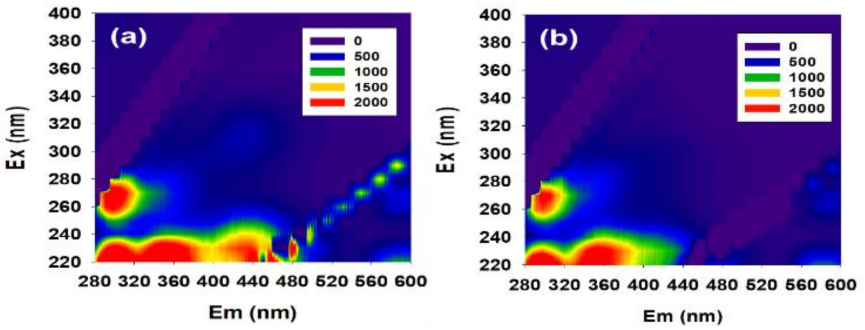

Fig. 10 The EEM spectra of (a) the raw water and (b) the neutralized water

operation. For instance, the rapid reduction was occurred in the 10 minutes and the reduction was almost sustained at relatively constant values

The organic matter in the metal plating wastewater is mainly composed of fatty oils and surfactants. There are various surfactants having anionic or cationic or nonionic properties. For instance, the sulfated fatty acid potassium has a molecular structure of $R\text{-}(CH_2)_8\text{-}CH\text{-}(CH_2)_7\text{-}COOK(\text{-}OSO_3K)$ and known as an anionic surfactant (Abbasov *et al.* 2013). The surfactants with anionic and cationic charges could transport to the boundary layer near the membrane surfaces due to the electrical force and involve in reactions in the boundary layer at the condition of elevated concentrations of rejected metal ions. The surfactant could also go through the ion-exchange membrane. However, molecular diffusivities of the surfactants would be small compared to the inorganic ions, therefore, their removals were low. In addition, increases of the DOC of the concentrates could affect inorganic fouling by complexing inorganics.

The organic compositions of the raw water and the neutralized water were examined with the Fourier-transform infrared (FTIR) spectroscopy. The water samples were collected from the feed and concentrates after the ED thus four water samples were analyzed as shown in Figure 9. The peaks of the model compounds of humic acid and alginic acids were also examined and presented in Figure 10. The characteristics peaks of humic acid and alginic acids were notified in the several wavelengths including O-H (3400nm), C=O and C=N bond (1578 nm and 1630 nm) and C-O bond (1388 nm and 1421 nm). The characteristic peaks were also observed in the sampled water, which indicating there were humic-like and polysaccharide-like organic matters in the raw and the neutralized water.

The 3-dimensional fluorescence spectra of EEM were also analyzed to understand characteristics of organic composition (Figure 11). The abscissa and ordinate represent the emission and excitation wavelength ranges, which are 280–600 nm and 220–400 nm, respectively. Several researchers investigated the specific fluorescence spectral signatures to elucidate the properties of organic matter (Coble *et al.* 1996, Hudson *et al.* 2007, Park *et al.* 2019). Intensity peaks located in Em 300 nm and Ex 270 nm and Em 360 nm and Ex 230 nm are in general recognized as soluble microbial by-product-like substances such as tryptophan and protein. Similarly, intensity peaks between Em 440 nm and Ex 270 nm and Em 430 nm and Ex 320 nm are known as indicative peaks of fulvic-like and humic-like substances. The raw wastewater and the concentrates from the ED operation showed strong peaks in between Ex wavelengths of 280 nm and 480 nm and Em wavelengths of 220 and 240 nm. In addition, a discrete peak at Ex 300 nm and Em 270nm. The characteristic peaks implied that the organic compositions in the raw and neutralized water were more likely soluble microbial products rather than humic-like substances since there were only vague trace of fluorescence in Em 430–440 nm and Ex 270–320 nm. The neutralization process seemed to reduce some organic compounds which expressed fluorescence in Em 440 nm and Ex 310 nm and in Em 440 nm and Ex 230 nm. However, most of parts of the neutralized water showed similar intensities to the raw water.

4. Conclusions

A wastewater from the metal plating industry was collected and the performance of ED for the removal of heavy metals and organic matter was evaluated using the raw water and the treated water by NaOH precipitation. The ED was effective to separate metal ions thus the operational time of 30 minutes was enough to reduce conductivity by 97.3% for the raw water and by 93% for the neutralized water. The removal of the hazardous heavy metal ions such as Cu, Ni, Cr, and Zn was great with respect to the percentage since the percent removal reached to more than 90%. To meet the standard for the wastewater effluent discharge, it was necessary to apply neutralization prior to ED. The high concentration of metal ions required the longer than 50 minutes of the ED operation. The composition of the organic matter in the metal plating wastewater was analyzed and the compositions were maintained in the raw and the concentrate samples. The neutralization process was capable to reduce some amounts of organic matter which exhibited fluorescence in Em 440 nm and Ex 310 nm and in Em 440 nm and Ex 230 nm. The organic matter in the raw water was reduced by the neutralization, which might enhance removal performance and mitigate organic fouling in the integrated system.

Acknowledgments

This subject is supported by Korea Ministry of Environment (MOE) AS "Technologies for the Risk Assessment & Management Program (2017000140006)". This paper was written as part of Konkuk University's research support program for its faculty on sabbatical leave in 2017.

References

Abbasov, V.M., Abd El-Lateef, H.M., Aliyeva, L.I., Qasimov, E. E., Ismayilov, I. T., Tantawy, A.H., and Mamedxanova, S.A. (2013), "Applicability of Novel Anionic Surfactant as a Corrosion Inhibitor of Mild Steel and for Removing Thin Petroleum Films from Water Surface", *Amer. Jour. Mater. Sci. Eng.*, **1**(2), 18-23. htteps://doi.org/10.12691/ajmse-1-2-1

Al-Amshawee, S., Yunus, M.Y.B.M., Azoddein, A.A.M., Hassell, D.G., Dakhil, I.H. and Hasan, H.A. (2020), "Electrodialysis desalination for water and wastewater: A review", *Chem. Eng. J.,* **380**(122231), 1-19. https://doi.org/10.1016/j.cej.2019.122231.

Banasiak, L.J., Kruttschnitt, T.W. and Schäfer, A. (2007), "Desalination using electrodialysis as a function of voltage and salt concentration", https://doi.org/10.1016/j.desal.2006.04.038.

Coble, P.G. (1996), "Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy", *Mar. Chem.*, **51**(4), 325-346. https://doi.org/10.1016/0304-4203(95)00062-3.

Choi, S.Y., K.Y. Park, Y. Yu, H.J. Kim, K.Y. Park, J.H. Kweon, J.W. Choe (2016), "Electrodialysis of groundwater with heavy metal and nitrate ions under low conductivity and effects of superficial velocities", *Desalination Water Treat*, **57**, 26741-26750.

Feng, Y., S. Yang, L. Xia, Z. Wang, N. Suo, H. Chen, Y. Long, B. Zhou, Y. Yu, (2019), "In-situ ion exchange electrocatalysis biological coupling (i-IEEBC) for simultaneously enhanced degradation of organic pollutants and heavy metals in electroplating wastewater", *J. Hazard. Mat.* **364**, 562-570, https://doi.org/10.1016/j.jhazmat.2018.10.068.

Hudson, N., Baker, A. and Reynolds, D. (2007), "Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—A review", *River Res. Appl.*, **23**(6), 631-649. https://doi.org/10.1002/rra.1005.

Iritani, E., Katagiri, N., Ishikawa, Y. and Cao, D. (2014), "Cake formation and particle rejection in microfiltration of binarymixtures of particles with two different sizes", *Sep. Puri. Tech.*, **123**, 214-220, http://dx.doi.org/10.1016/j.seppur.2013.12.033.

Lafi, R., W. Mabrouk and A. Hafiane, (2019), "Removal of Methylene blue from saline solutions by adsorption and electrodialysis", *Membr. Water Treat.*, **10**(2) 139-148.

Martí-Calatayud, M.C., M. García-Gabaldón and V. Pérez-Herranz, (2018), "Mass Transfer Phenomena during Electrodialysis of Multivalent Ions: Chemical Equilibria and Overlimiting Currents", *Appl. Sci.*, **8**(9), 1566. https://doi.org/10.3390/app8091566.

Min, K.J., Choi, S.Y., Jang, D., Lee, J., Park, K.Y. (2019), "Separation of metals from electroplating wastewater using electrodialysis", *Energy Sources, Part A Recovery, Utilization, Environ. Effects*, **41**(20), 2471-2480. https://doi.org/10.1080/15567036.2019.1568629.

Park, K. Y., Cha, H. Y., Chantrasakdakul, P., Lee, K., Kweon, J. H. and Bae, S. (2017), "Removal of nitrate by electrodialysis: effect of operation parameters", *Membr. Water Treat.*, **8**(2) 201-210, http://doi.org/10.12989/mwt.2017.8.2.201.

Park, K.Y., Yu, Y.J., Yun, S.J. and Kweon, J.H. (2019), "Natural organic matter removal from algal-rich water and disinfection by-products formation potential reduction by powdered activated carbon adsorption", *J. Environ. Management*, **235**, 310-318. https://doi.org/10.1016/j.jenvman.2019.01.080.

Tanaka, Y. (2002), "Current density distribution, limiting current density and saturation current density in an ion-exchange membrane electrodialyzer", *J. Memb. Sci.*, **210**(1), 65-75. https://doi.org/10.1016/S0376-7388(02)00376-9.

Mohammadi, T., Moheb, A., Sadrzadeh, M., Razmi, A. (2005), "Modeling of metal ion removal from wastewater by electrodialysis", *Separation Purification Technol.*, **41**(1), 73-82.

Fu, F. and Wang, Q. (2011), "Removal of heavy metal ions from wastewaters: a review", *J. Environ. Manag.*, **92**(3), 407-418. https://doi.org/10.1016/j.jenvman.2010.11.011.

Huang, C., T. Xu, Y. Zhang, Y. Xue, G. Chen, (2007), "Application of electrodialysis to the production of organic acids: state-of-the-art and recent developments", *J. Memb. Sci.*, **288**(1-2) 1-12, https://doi.org/10.1016/j.memsci.2006.11.026.

Oztekin, E. and Altin, S. (2016), "Wastewater treatment by electrodialysis system and fouling problems", *Turkish Online J. Sci. Technol.*, **6**(1), 91-99. https://www.tojsat.net/journals/tojsat/articles/v06i01/v06i01-14.pdf.

Chung, H.J., Cho, S.H. and Ku, B.H. (2003), "Collection of valuable metal using electroplating method", *J. Nakdong River Environ. Research Institute*, **8**, 47-53.

Strathmann, H. (2010), "Electrodialysis, a mature technology with a multitude of new applications", *Desalination*, **264**(3), 268-288. https://doi.org/10.1016/j.desal.2010.04.069.

Sarker, B., Papageorgiou, G.D., Silva, R., Zehnder, T., Gul-E-Noor, F., Bertmer, M., Kaschta, M., Chrissafis, K., Detscha, R. and Boccaccini, A.R. (2014), "Fabrication of alginate-gelatin crosslinked hydrogel microcapsules and evaluation of the microstructure and physico-chemical properties", *J. Mater. Chem. B.*, **2**, 1470-1482. https://doi.org/10.1039/C3TB21509A.

Van der Bruggen, B., Koninckx, A. and Vandecasteele, C. (2004), "Separation of monovalent and divalent ions from aqueous solution by electrodialysis and nanofiltration", *Water Res.,* **38**, 1347-1353. https://doi.org/10.1016/j.watres.2003.11.008.

Woźniak, M.J. and Prochaska, K. (2014), "Fumaric acid separation from fermentation broth using nanofiltration (NF) and bipolar electrodialysis (EDBM)", *Sep. Purif. Technol.*, **125**(7) 179-186, https://doi.org/10.1016/j.seppur.2014.01.051.

Zhang, X., Fan, L. and Roddick, F.A. (2014), "Feedwater coagulation to mitigate the fouling of a ceramic MF membrane caused by soluble algal organic matter", *Sep. Puri. Tech.*, **133**, 221-226, http://dx.doi.org/10.1016/j.seppur.2014.06.053.

Gherasim, C.V., Křivčík, J. and Mikulášek, P. (2014), "Investigation of batch electrodialysis process for removal of lead ions from aqueous solutions", *J. Chem. Eng.*, **256**, 324-334. https://doi.org/10.1016/j.cej.2014.06.094.

Scarazzato, T., Buzzi, D.C., Bernardes, A.M. and Espinosa, D.C.R. (2015), "Treatment of wastewaters from cyanide-free plating process by electrodialysis", *J. Clean Prod.*, **91**, 241-250. https://doi.org/10.1016/j.jclepro.2014.12.046.

Walker, W.S., Kim, Y. and Lawler, D.F. (2014), "Treatment of model inland brackish groundwater reverse osmosis concentrate with electrodialysis—Part II: sensitivity to voltage application and membranes", *Desalination*, **345**, 128-135. https://doi.org/10.1016/j.desal.2014.04.026.

CC