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Effects of organic concentrations on inorganic precipitation during electrodialysis of metal plating wastewater

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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 anionic 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.

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. Several treatment processes including precipitation, adsorption, ion-exchange, and reverse osmosis filtration, are employed to remove the harmful ions from the wastewater. 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 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 during ion transport due to the electrical forces. The ED is in usual 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

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recovered. Therefore, the high efficiency of ED is essential for the success of the removal and recovery of the heavy metal.

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 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. During the precipitation, organic matter could play roles for the crystallization processes. 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 analyzed water qualities were summarized in Table 1. The pH of the raw water was substantially acidic and the conductivity was also very high. The neutralization shows higher removal of Cu with approximately 93%, compared to the 62% removal of Ni and 65% removal of Zn. The conductivity was reduced only 55% 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) concentration was reduced 45.8% by neutralization.

Table 1. Key water qualities of the raw and neutralized wastewater.

	pH (-)	Conductivity (mS/cm)	Cu (mg/L)	Ni (mg/L)	Zn (mg/L)	DOC (mg/L)
Raw	2.0	18.4	419.0	185.4	21.6	153.0
Neutralized	7.6	8.3	30.6	70.5	7.5	82.9

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 cm2, 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 for five minutes and increased to 30 volts for the raw water and to 50 volts for the neutralized water. The limiting current was occurred at 10 volts with a value of 21.6 mA/cm2 for the raw water and at 46 volts with a value of 60.0 mA/cm2 for the neutralized water. The ED operation was performed at the voltage for the 80% of the limiting currents.

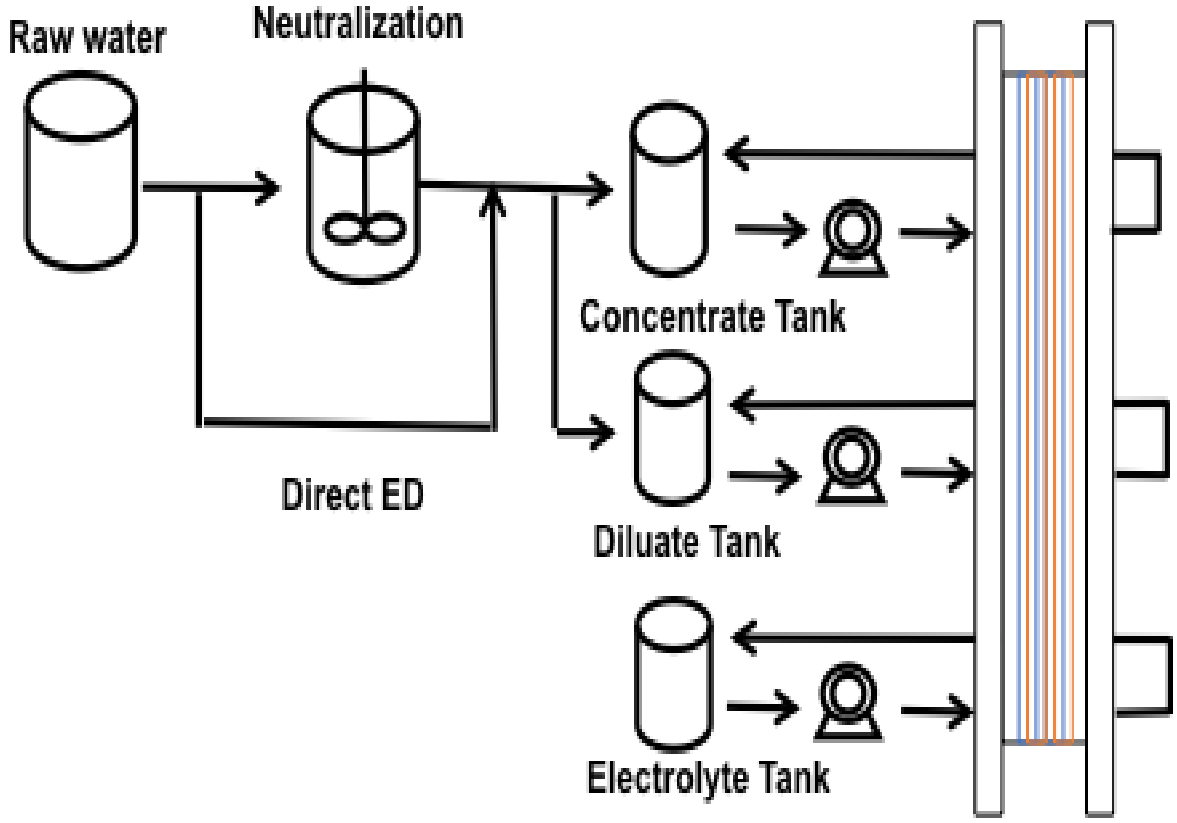

Figure 1. Schematic diagram of neutralization and ED processes in this study

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., USA). The electrical conductivity and pH of the solution were measured using an Orion 5 Star instrument (Thermo Fisher Scientific Inc., USA).

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. 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 about 30 minutes of operation was conducted as shown in Figure 2. The conductivity of the raw was 18.4 mS/cm and that was decreased to 0.53 mS/cm after the 30 minutes of the operation. The reduction rate of the conductivity was 97.1%. As shown in Table 1, the neutralization removed about 55% of the conductivity, thus the initial conductivity of the treated water was 8.3 mS/cm 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 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, Choi et al, 2017, Min et al, 2019) The removal rate with the neutralized water was achieved with short time due to the high applied voltage.

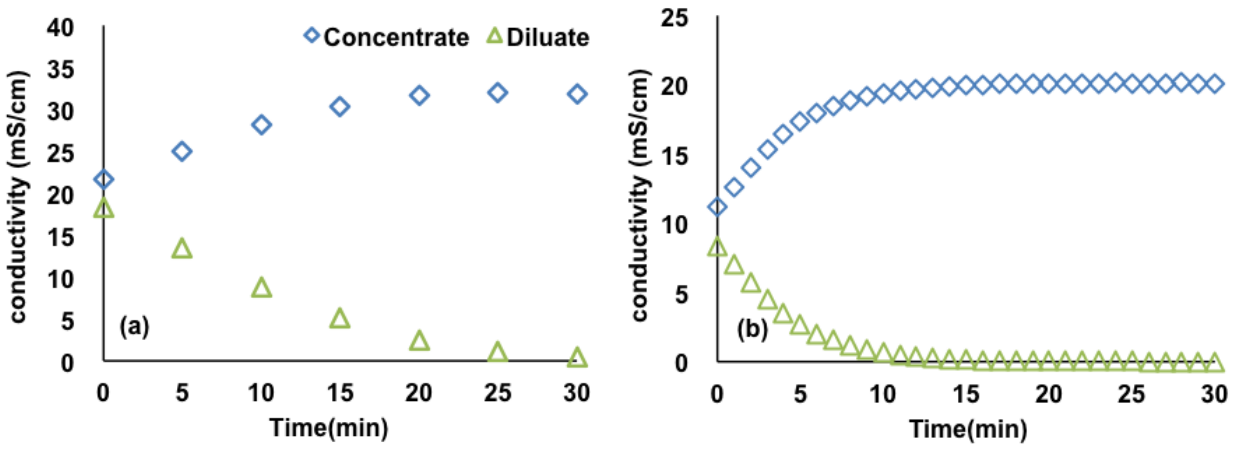

Figure 2. Changes of conductivity during ED. (a) the raw water, (b) the neutralized water

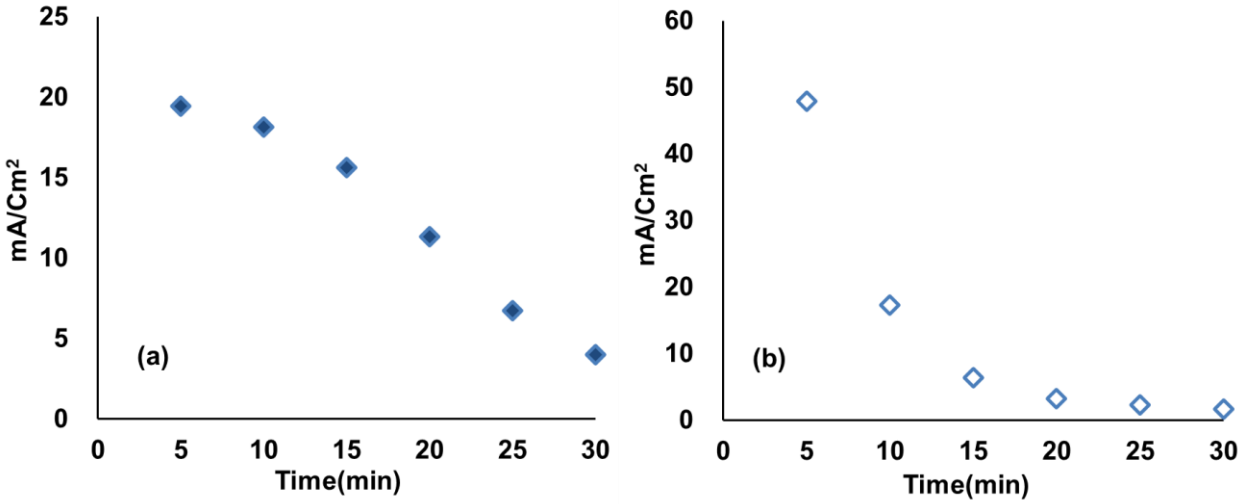

Figure 3. Changes of current density during ED. (a) the raw water, (b) the neutralized water

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 30.6 mg/L for Cu, 70.5 mg/L for Ni, 0.2 mg/L for Cr, and 7.5 mg/L for Zn. The Cr concentration after the neutralization already met effluent standard of discharge in Korea. The neutralization process was very effective to remove chromium ions from the wastewater. The reduction rates with 30 minutes of ED operation were 99.1% for Ni, 97.8% for Cu, and 91.1 % for Zn. The Cu and Zn was effectively removed by ED. Only about 20 minutes of ED operation was enough to satisfy the effluent standard for discharge. However, the Ni ions were difficult to lower the concentration below the effluent standard.

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	30.6 (-)	70.5 (-)	0.190 (-)	7.5 (-)
5	13.8 (55.0%)	23.5 (66.7%)	0.065 (65.8%)	2.86 (61.7%)
10	3.91 (87.2%)	3.70 (94.8%)	0.070 (63.2%)	0.94 (87.4%)
15	1.09 (96.4%)	0.90 (98.7%)	0.040 (79.0%)	0.54 (92.8%)
20	0.65 (97.9%)	0.68 (99.0%)	0.030 (84.2%)	0.51 (93.2%)
25	0.51 (98.3%)	0.57 (99.2%)	0.025 (86.8%)	0.53 (93.0%)
30	0.66 (97.8%)	0.62 (99.1%)	Not available	0.67 (91.2%)
Effluent standard for discharge	1.0	0.1	0.5	1.0

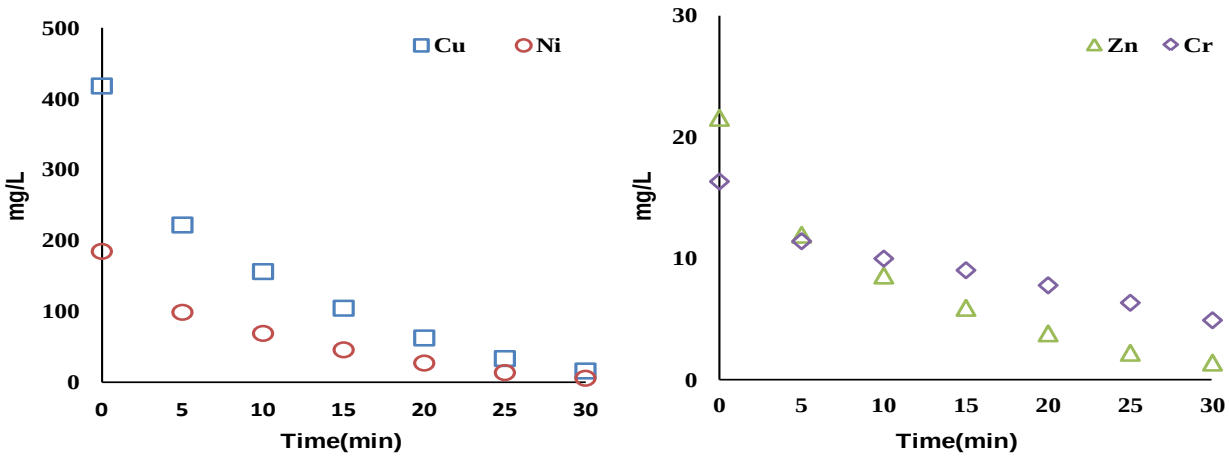

Figure 4. Removal of metal ions during ED operation for the raw water. (a) Cu and Ni, (b) Zn and Cr

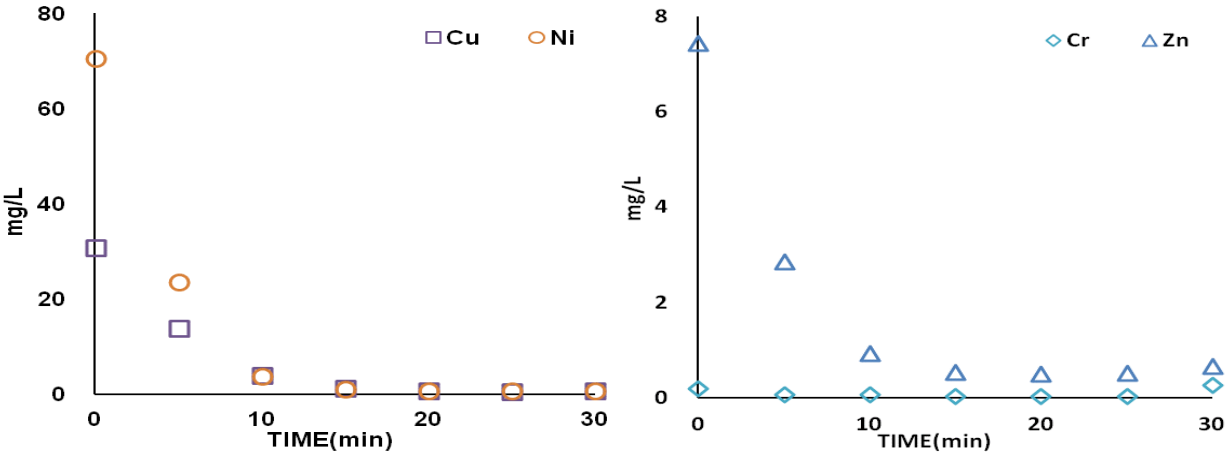

Figure 5. Removal of metal ions during ED operation for the neutralized water. (a) Cu and Ni, (b) Zn and Cr

3.3 Effects of organic matter in ED operation

Although a majority of the metal plating wastewater was inorganic ions, some organic matter were also present in the wastewater. 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 about 42% of organic matter of the raw water, so the initial DOC concentration in the neutralized water was 89.0 mg/L. The reduction of the organic matter with the neutralized water was greater at the all the operation time than that with the raw water.

In addition, the reduction of the DOC concentration was substantial until the 10 minutes of ED operation and the reduction was almost constant.

The organic compositions of the raw water and the neutralized water were examined with the Fourier-transform infrared (FTIR) spectroscopy.

Table 4. 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	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%)

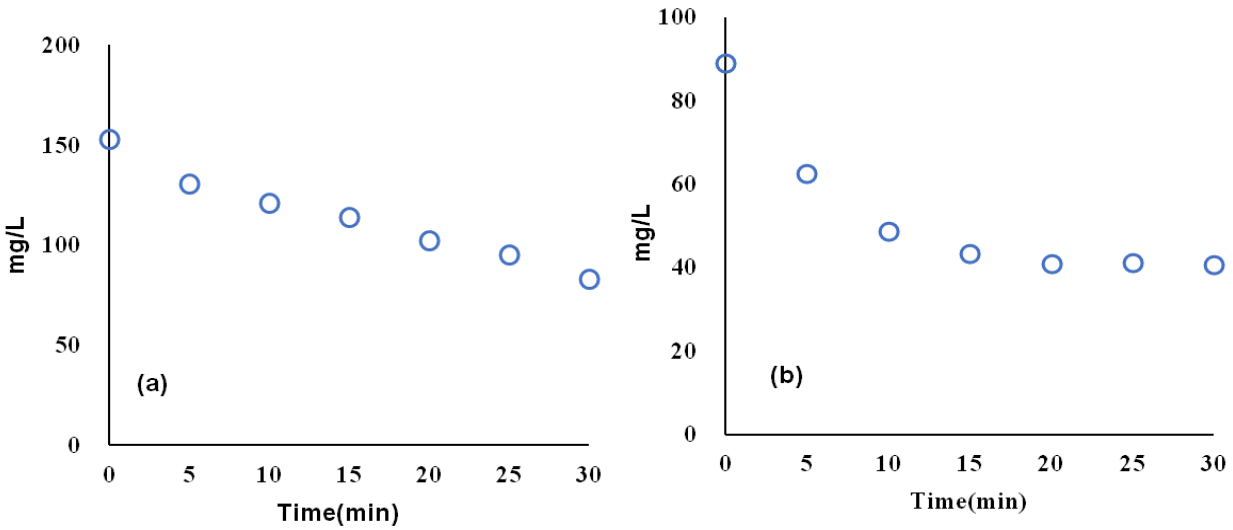

Figure 6. Reduction of DOC during ED. (a) the raw water and (b) the neutralized water.

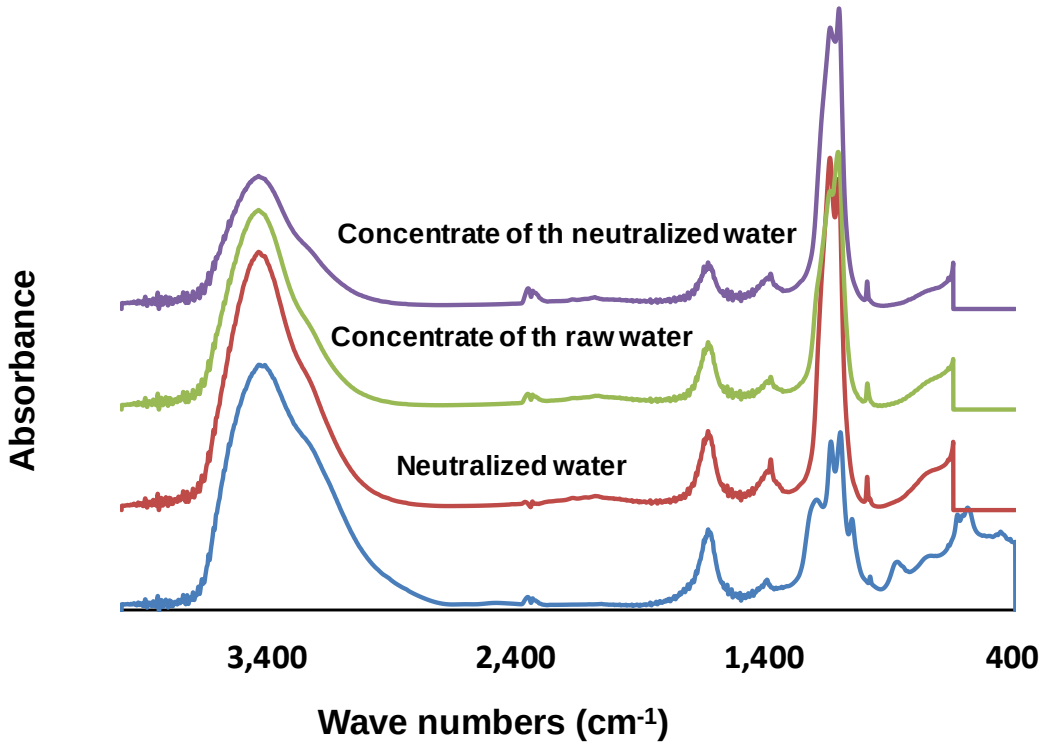

Figure 7. The FTIR spectra of the four different water samples.

4. CONCLUSIONS

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 water and the treated water by NaOH precipitation. The ED was effective to separate metal ions thus the operational time of 30 minutes and 8 volts was enough to reduce conductivity of the raw water and operational time of 10 minutes and 40 volts was able to reduce the conductivity of 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%. However, the effluent standard for discharge was not satisfied for the raw water by only ED and was met with the integrated processes of neutralization and ED. The organic matter removal was low compared to the inorganic metal ions for the raw water and the neutralized water. The composition of the organic matter in the metal plating wastewater was analyzed and the main compositions were maintained in the four samples.

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