

Article

# Effect of Chloride Ions on Electro-Coagulation to Treat Industrial Wastewater Containing Cu and Ni

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**Abstract:** A series of experiments with different NaCl concentrations added to the PCB (printed circuit board) wastewater were prepared to investigate the chloride effect on the formation of aluminum floc and removal efficiency of Cu and Ni. The effects of pH, current density, and different concentration of NaCl were studied and the results are discussed. Results imply that chloride ions are favored to avoid the passivation of the aluminum anode in the EC (electro-coagulation) system. Chloride ions used as the electrolyte can facilitate the release of  $Al^{3+}$ , which results in the current efficiency of over 100% in the EC system. For the PCB factory's wastewater, the EC system could remove  $Cu^{2+}$  and  $Ni^{2+}$  effectively (both Cu and Ni concentration of treated wastewater was less than 1.0 mg/L within three minutes). PCB wastewater's pH value could maintain stably about 9.0 in the EC system when the initial pH value was around 2.5. The estimated electricity consumption for treating PCB wastewater by the EC process was about 0.894 kWh for each meter of cubic wastewater.

**Keywords:** copper; current efficiency; electro-coagulation; nickel; wastewater

## 1. Introduction

The electro-coagulation (EC) technique has received considerable attention to remove heavy metals from the industrial wastewater for decades. Several researchers expect to use the EC process to replace the traditional chemical coagulation [1–3]. The advantages of EC compared to the conventional chemical coagulation include simple operation, effective and rapid removal, extensive pH range, and acceptable cost [4–7]. To create the coagula, the attractive force with Van der Waals must overcome the repulsive force within the double layer of the suspending particles. By adding the coagulant, agents can reduce the electrostatic repulsion and further decrease the distance of the electrical double-layer [8,9]. The EC approach employs the same coagulation mechanism as the above. In an EC system, the electro-dissolution of sacrificial anodes forms complexed species with hydroxide ions, which act as coagulant agents to separate pollutants from the wastewater. The extreme reactions of EC technology include (1) metallic ions generated by the sacrificial anode (Al or Fe is commonly used) in the reaction tank, (2) hydroxide ions generated by cathode to form floc, (3) the occurrence of coagulation precipitation (e.g.,  $Al(OH)_3$ ) and (4) the metallic and organic pollutants which could be separated from the aqueous phase by such coagula [10,11]. Furthermore, the hydrogen bubble generated in the

cathode can be used to achieve the effect of agitation or flotation. Hence, the coagulation purpose can be achieved without adding chemicals or mechanical agitation during the EC process. The above reaction rates are fast (usually takes only a few minutes). To consider all kinds of organic and inorganic pollutants, the EC method can be used to remove them effectively [1,2,12–15]. However, the operation cost of the EC method might be relatively higher due to its electricity consumed; therefore, to be competitive with the traditional chemical coagulation method, more researches need to be explored to obtain proper and effective operation parameters.

To control all kinds of chemical reactions smoothly during electrochemical methods to process waste material, the electrical potential or current control is one of the essential operating parameters. Generally, the electrical potential that the EC method needs to surmount to generate current among electrode plates includes balance potential, concentration over-potential, activation over-potential, and ohm over-potential [2,16]. To avoid the concentration, activity, and electrical polarization is beneficial to reduce the voltage, save energy, and let the reaction happen smoothly. Accordingly, the addition of electrolytes in wastewater can increase conductivity (i.e., a decrease of the high polarization) and reduce the voltage to achieve energy-saving. The commonly used electrolyte includes KCl, NaCl, and NaNO<sub>3</sub>. The chloride ions will have pitting corrosion on the metallic anode plate, which can avoid the generation of the passivation layer on the anode plate surface and the subsequent resistance polarization [17–21]. Based on previous studies under the operation condition of a fixed voltage, the EC system can maintain at a current stable state by adding nitrate ions, the Al ions dissolved from the anode, and OH<sup>-</sup> generated on the cathode. However, due to the over-rise of pH value (i.e., pH over 9.0), Al(OH)<sub>4</sub><sup>-</sup> thus becomes the main species and floc cannot be formed.

In contrast, by adding chlorine salt in the EC system, the solution pH shows a trend of first ascending and later descending and then maintains at a steady range of 9–10. As a result, Al(OH)<sub>3</sub> floc can be formed, and heavy metals can be removed quickly and effectively [19]. Accordingly, the chloride ions have been chosen as the electrolyte in the EC system to treat the printed circuit board (PCB) wastewater in this study.

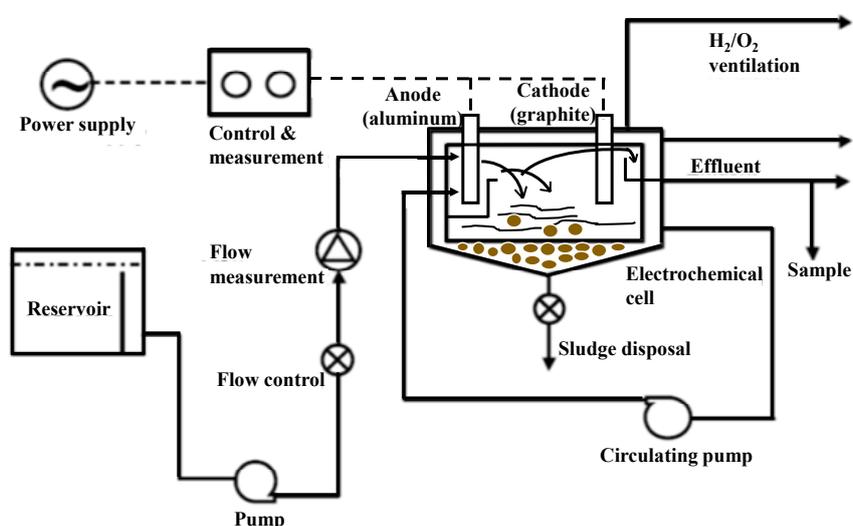
The printed circuit board (PCB) is the essential component in most electrical and electronic devices, whose primary function is to support the electrical units and link the electrical circuits [22]. The PCB fabricating processes include edge trimming, copper cladding, protective film, drilling pad, overlaying, and scraping plate, which will produce acidic/alkali wastewater with a high concentration of inorganic/organic pollutants [23–25]. Water consumption can be as high as 1.5 m<sup>3</sup> per m<sup>2</sup> of the board processed [26]. In Taiwan, more than 100,000 tons of PCB are generated annually [27]. Such complicated sewage is one of the most common factory wastewaters. Moreover, these metallic ions exist in a stable state of coordination complexes with benzotriazole, 2-aminothiazole, and other organic ligands, which significantly influences the treatment effectiveness [28]. The discharge of untreated PCB wastewater will bring a massive threat to the environment and result in a waste of valuable resources [29,30]. The discharge standard of Cu and Ni is 3 mg/L and 1 mg/L, respectively, in Taiwan, and it is hard to meet such criteria dealing with PCB wastewater. Consequently, it is very urgent to develop a cost-effectiveness and sustainable remediating technique for PCB wastewater.

In this study, a series of experiments with different concentrations of NaCl added to the wastewater (different initial pH values of sewage as well) were prepared to investigate the chloride effect on the formation of aluminum floc. Under different current densities, the relationship among the release amount of aluminum ions, voltage change, and the consumed electricity of the EC system was established. Moreover, wastewater containing Cu and Ni from individual PCB plants was used for the EC process to observe the removal efficiency of heavy metals. Through this study, the practical operational parameters of the EC process can be obtained for further application.

## 2. Materials and Methods

### 2.1. Experimental and Equipment

The EC experimental setup is shown in Figure 1. A polyvinylchloride (PVC) reaction tank (total volume of reaction tank of 250 cm<sup>3</sup>) was set up, with a metallic aluminum plate used as an anode. In the present study a graphite plate was used as a cathode with an area of 82 cm<sup>2</sup>. NaCl added in the solution for this study was purchased from Riedel-de Haen, USA, with a purity of 99.6%. Sulfuric acid (Merck, >95%) and NaOH (Sigma-Aldrich, >97%) were used for acidic or basic adjustment of the solution. During the operation, the solution within the reaction tank was internally circulated with a quantitative motor (with flow rate adjusted to 250 cm<sup>3</sup>/min) to ensure that the solution was well mixed. A programmable power supply (DC) was employed to provide the current to EC reactions. The DC power supply is manufactured by MOTTECH INDUSTRIES INC with a model number of PPS1002F/CE/MT (0 to 18 V, 0 to 4 A), which can read the voltage values.



**Figure 1.** Schematics of electro-coagulation (EC) experimental setup [20].

### 2.2. Experimental Method

A constant current was applied at 0.5 A, 1.0 A, 1.5 A, and 2.0 A (i.e., the current densities were 60.98 A/m<sup>2</sup>, 121.95 A/m<sup>2</sup>, 182.93 A/m<sup>2</sup>, and 243.90 A/m<sup>2</sup>, respectively). The high current densities in subsequent figures were represented individually by integral values of 60 A/m<sup>2</sup>, 120 A/m<sup>2</sup>, 180 A/m<sup>2</sup> and 240 A/m<sup>2</sup>. To investigate the effect on voltage and consumed electricity by chlorine ions in the wastewater, different concentrations of NaCl were controlled in the EC system, namely, 1.00 g/L, 1.75 g/L, and 2.5 g/L, then operated for 10 min. An appropriate amount of NaCl was selected according to the previous experimental results, then EC was operated for 20 min. During the EC process, the dissolved amount of Al ion was recorded to establish the relationship between Al release magnitude and current density. Meanwhile, the corrosion phenomenon by chlorine ions during the EC process could be understood by the weight loss of aluminum anode. Since the pH of the solution mainly controls the chemical coagulation, the pH of the solution was monitored (pH meter, Suntex, SP-701) during the EC process to evaluate the floc formation.

In order to understand the practical feasibility of the EC technique for wastewater containing heavy metals, Cu and Ni from a real plant (PCB process) were used for the experiment. Within the operation time, the voltage and pH value of wastewater was determined. Also, the conductivity was measured (Conductivity meter, Suntex, SC-170). Following a 20-min EC treatment, the formed flocs precipitated for 30 min. The upper supernatant was sampled to determine the concentration of Cu and Ni by inductively coupled plasma atomic emission spectrometer (Thermo, IRIS Intrepid II XSP).

All water samples were triple repeat analyzed, and the average value was taken to ensure the water sample stability.

### 3. Results and Discussion

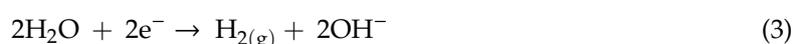
#### 3.1. Mechanism of EC

When metallic Al is used as the anode and graphite as the cathode in an EC system, the initial reactions are generated as the following Equations (1)–(4):

(a) Oxidation reactions at the anode:



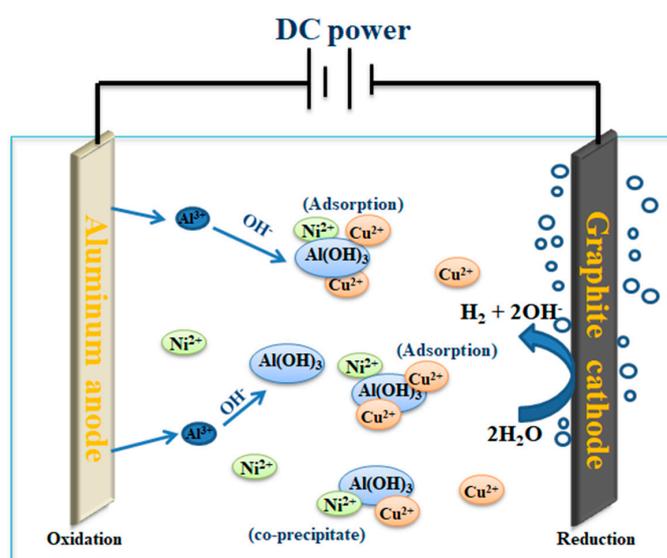
(b) Reduction reaction at the cathode:



(c)  $\text{Al}^{3+}$  ions generated at the anode will form  $\text{Al}(\text{OH})_3$  floc in the solution with  $\text{OH}^{-}$  generated at the cathode:



Theoretically,  $\text{Al}^{3+}$  ions will have different electrolytic forms such as  $\text{Al}(\text{OH})_2^{2+}$ ,  $\text{Al}(\text{OH})_2^{+}$ ,  $\text{Al}(\text{OH})_4^{-}$ , etc., along with the pH change of the solution. Al polymer-form hydrolytic products, such as  $\text{Al}_2(\text{OH})_2^{4+}$ ,  $\text{Al}_3(\text{OH})_4^{5+}$ ,  $\text{Al}_6(\text{OH})_{15}^{3+}$ ,  $\text{Al}_7(\text{OH})_{17}^{4+}$ ,  $\text{Al}_8(\text{OH})_{20}^{4+}$ ,  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{5+}$  and  $\text{Al}_{13}(\text{OH})_{34}^{5+}$ , will be generated as well [31,32]. The  $\text{Al}(\text{OH})_3$  floc will adsorb contaminants in the wastewater, which can remove contaminants effectively after precipitation. Accordingly, the optimum operating parameters of the EC system should be ensured to be applicable. For the actual condition of this study, the  $\text{Al}^{3+}$  ions can be generated at the anode under the aluminum anode was used in the electro-coagulation operation, which can form a hydroxide of  $\text{Al}(\text{OH})_3$  and easily remove the heavy metals from the wastewater. The pollutants in wastewater can be removed through adsorption, co-precipitation, and other reaction mechanisms [16]. Figure 2 illustrates a schematic diagram of the EC technique mechanism for the removal of Cu(II) and Ni(II) from industrial wastewater.



**Figure 2.** Schematic diagram of the EC technique mechanism for the removal of Cu(II) and Ni(II) from industrial wastewater.

### 3.2. The Effect of NaCl on Voltage and Consumed Electricity

Figure 3 shows the consumed power (watts) as a function of current density ( $A\ m^{-2}$ ) under different dosage concentrations of NaCl. It can be seen that the current density increased with significant growth of the consumed electricity. According to Ohm's law, the voltage is proportional to current. The electrical potential (voltage) is mainly ohm over-potential of solution (that is, the voltage needed to surmount solution resistance)  $\eta_{IR}$  or called IR-drop (5):

$$\eta_{IR} = \frac{Id}{AK} \quad (5)$$

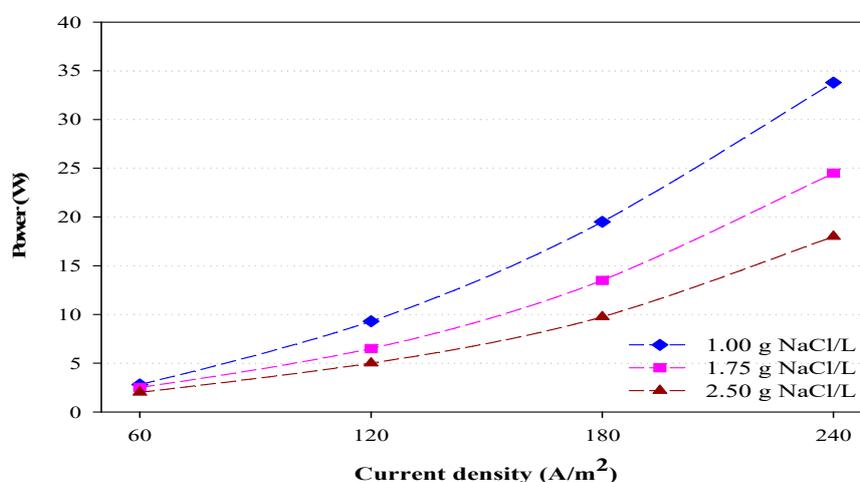
where I is current, d is the spacing between the electrode plate, A is the surface area of the electrode plate, and K is conductivity. Since I, d and A are all constant values,  $\eta_{IR}$  is reversely proportional to conductivity K. The NaCl dosage increases conductivity (K value is more substantial); the voltage needed for the reaction is thus lower.

Since the consumed electricity is related to power P (Unit: W), 1 degree of electricity is 1 kWh (kilowatt-hour):

$$P = VI \quad (6)$$

where V is the voltage, and V (voltage) is proportional to P (power).

According to the above equation, the increased voltage enhances the consumed electricity in the EC system. To consider the influence of chloride ions, it could be noticed that higher NaCl dosage obtained lower consumed power under the same current density. This means the higher electrolyte concentration (high NaCl dosage) created higher electrical conductivity, which resulted in lower voltage under the same current density.

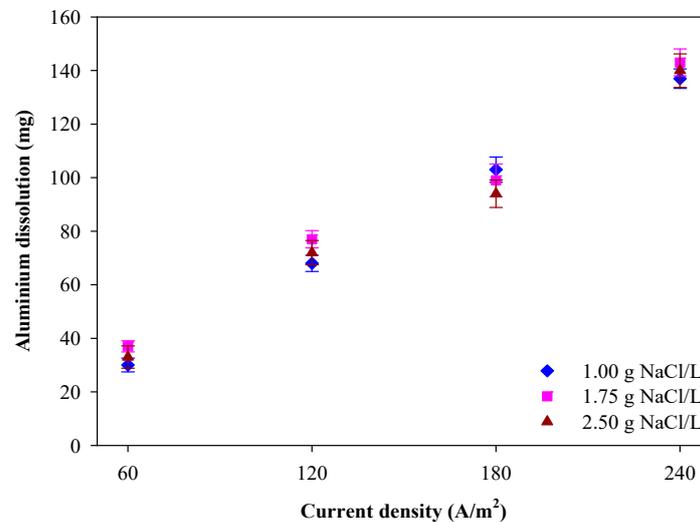


**Figure 3.** Consumed electricity (watts) as a function of current density ( $A/m^2$ ) under different NaCl concentrations.

### 3.3. Aluminum Dissolved Amount and Current Efficiency

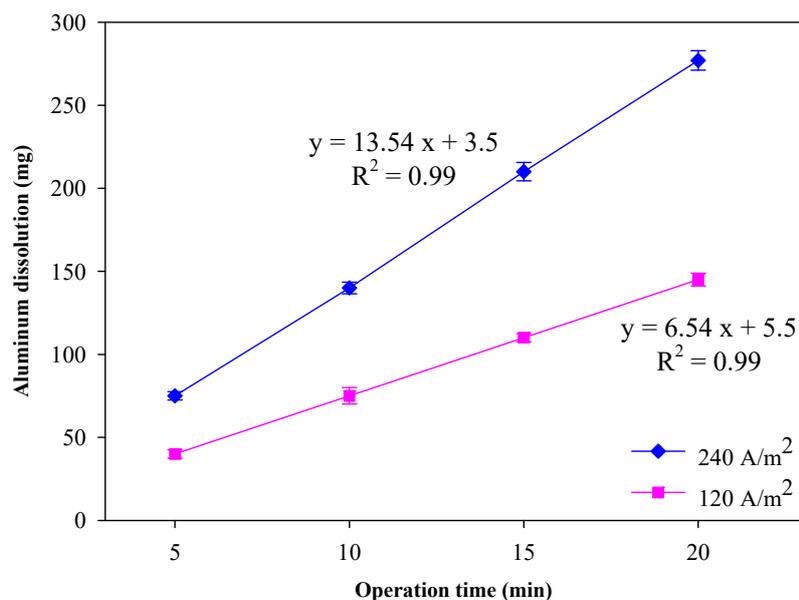
Figure 4 showed the relationship between the Al dissolution amount and current density under different NaCl concentrations. From the figure, it could be seen that Al dissolution was proportional to the current density and is independent of NaCl concentration. Based on equation (1), the Al anode will release aluminum ions due to oxidation reaction (i.e., lose electrons). Consequently, more electrons involved in the EC system cause more free Al ions. To consider the effect of chloride ions,  $Cl^-$  ions could avoid the formation of the oxide layer on the anode surface. When the oxide layer is formed at the anode, the chloride ions could react with the oxide layer and decompose such a high-resistance layer. Under the same current density, high NaCl concentration only decreased the voltage rather than increasing the Al dissolution amount. It can be attributed that the chloride ions prevent the interface of

the aluminum anode from impurities that hinders the oxidation of aluminum dissolution. A particular concentration of chloride could maintain the clean surface of the anode. Namely, the chloride effect becomes insignificant when the level of chloride ions is over the proper parameter.



**Figure 4.** Relationship between Al dissolution amount and current density under different NaCl concentrations.

Figure 5 shows the relationship between Al dissolution amount and operation time under different NaCl concentrations. It could be observed that the Al dissolution amount was proportional to operation time since the number of electrons (current multiplied time) controlled the extent of electrochemical reaction, which illustrated the dissolution amount of Al associated with operational time. Meanwhile, the higher current density led to the linear equation (i.e., the dissolution rate of Al is quicker), which meant more flocs could be obtained in the shorter operational time. This phenomenon implies that the formation of flocs in the EC system was associated directly with the number of electrons from the electrochemical reaction. The Al dissolution being faster caused more electricity to be consumed.



**Figure 5.** Relationship between Al dissolution amount and operation time under different NaCl concentrations.

Table 1 lists the Al dissolved amount and current efficiency under different operation currents and NaCl concentrations. To consider the current efficiency of the EC system, it can be computed as the following (7) and (8):

$$\Phi = \frac{m_{Al(R)}}{m_{Al(T)}} \times 100\% \quad (7)$$

$$m_{Al(T)} = \frac{ItM}{nF} \quad (8)$$

where  $m_{Al(R)}$  and  $m_{Al(T)}$  are the actual and theoretical weight loss of Al anode, respectively, and the term  $\Phi$  is the current efficiency. The value of  $m_{Al(T)}$  is calculated from Faraday law,  $I$  is current,  $t$  is reaction time,  $M$  is atomic weight,  $n$  is valence number, and  $F$  is the Faraday constant of 96,500 coulombs. From the data in Table 1, it could be seen that current efficiencies were all greater than 100%. Theoretically, the current efficiency of the electrochemical reaction is less than 1.0 (<100%) because not all electrons are involved in the Al dissociation. However, many EC research results showed that the current efficiency was more significant than 1.0 (>100%). If both cathode and anode are used with Al material, current efficiency can even be over 1.5. Some researchers called this phenomenon “super faradaic efficiencies” [33]. This specific situation could be attributed to the “pitting corrosion reaction” of chloride ions on the anode [34]. Such a reaction might be attributed to the following reactions (9)–(11).



The chloride ions can transform to HOCl that oxide the aluminum atom to produce  $Al^{3+}$  ions. The HOCl is a more potent oxidant than chlorine under standard conditions.

**Table 1.** The Al dissolved amount and current efficiency under different operation currents and NaCl concentrations.

Current (A)	NaCl (g L <sup>-1</sup> )	V <sub>avg</sub> (V)	m <sub>Al(R)</sub> (mg)	Φ (%)
0.5 (60 A/m <sup>2</sup> )	1.00	5.24	28	100
	1.75	3.82	35	125
	2.50	3.05	33	118
1.0 (120 A/m <sup>2</sup> )	1.00	9.27	66	118
	1.75	6.15	75	134
	2.50	4.89	71	127
1.5 (180 A/m <sup>2</sup> )	1.00	13.10	102	122
	1.75	9.06	98	117
	2.50	6.73	93	111
2.0 (240 A/m <sup>2</sup> )	1.00	16.70	138	123
	1.75	12.03	144	129
	2.50	8.81	141	126

### 3.4. The pH Variation of Wastewater during EC Operation

Figure 6 showed the pH variation with operational time under a current density of 120 A/m<sup>2</sup> and 1.75 g/L NaCl. The flocs formed effectively in the EC system should be maintained at pH ranging from 6.0 to 9.0, according to equation 4. In this study, the PCB wastewater usually has a low pH value. From Figure 6, it could be noticed that the initial pH value of the sewer was 2.0, 2.5, 3.0, and 7.0, respectively. After a 20-min operation, most pH values of wastewater, except the initial pH of 2.0, could be increased up to around 9.0. The main factor that causes the rise of pH based on equation (3) is the contribution of OH<sup>-</sup> generated from the reduction reaction of the cathode. As the wastewater was

filled with too much acid, the EC system would fail due to the low final pH of sewage in the EC system (i.e., no flocs will be formed).

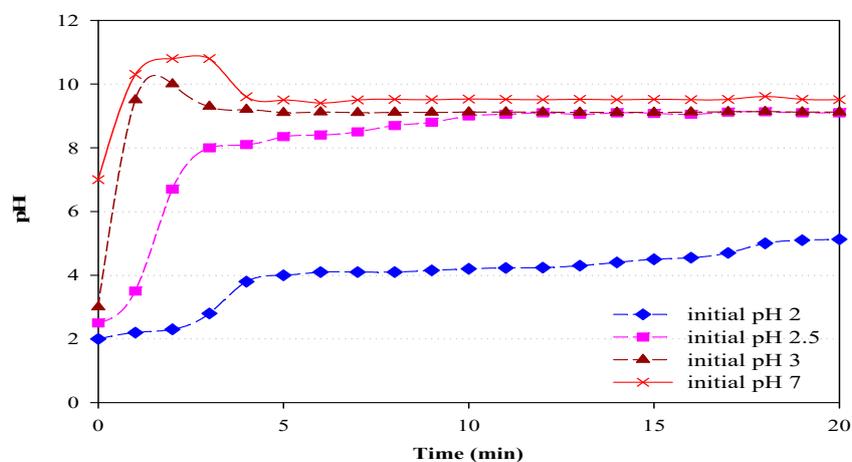


Figure 6. pH variation with operational time under a current density of  $120 \text{ A/m}^2$  and  $1.75 \text{ g/L NaCl}$ .

### 3.5. The Removal Efficiency of Cu and Ni Wastewater by EC Process

Figure 7 shows the removal efficiency of Cu and Ni wastewater after EC treatment under the current of  $1.0 \text{ A}$  and  $1.75 \text{ g/L NaCl}$ . The initial concentration of Cu and Ni in the PCB wastewater was about  $10 \text{ mg/L}$  and the initial pH was  $3.0$ . After  $10\text{-min}$  EC treatment, the final pH was  $7.76$ ; the average voltage was  $6.27 \text{ V}$ , anode Al weight loss was  $70 \text{ mg}$ , and current efficiency reached  $117\%$ . According to Figure 7, it could be observed that the heavy metal concentrations of Cu and Ni were both reduced to below  $1.0 \text{ mg/L}$  after a  $3\text{-min}$  operation; both heavy metals could not be detected after  $8\text{-min}$  treatment. The result shows that Cu and Ni in the PCB wastewater could be entirely removed under such an EC system and meet regulatory standards. Finally, the determined results were compared with the previous report which is shown in Table 2. Based on the results described in Table 2, it can be noted that the EC has tremendous potential to transform emerging technology and traditional approaches to wastewater management. Here, the EC is sufficient to recycle water for industrial or domestic recycling because this EC mechanism completely eliminates Cu and Ni compared to other reports. Moreover, based on data regarding the electricity consumption, the cost of electricity consumed for this processing could be estimated at around  $0.894 \text{ kWh}$  each meter cubic of wastewater.

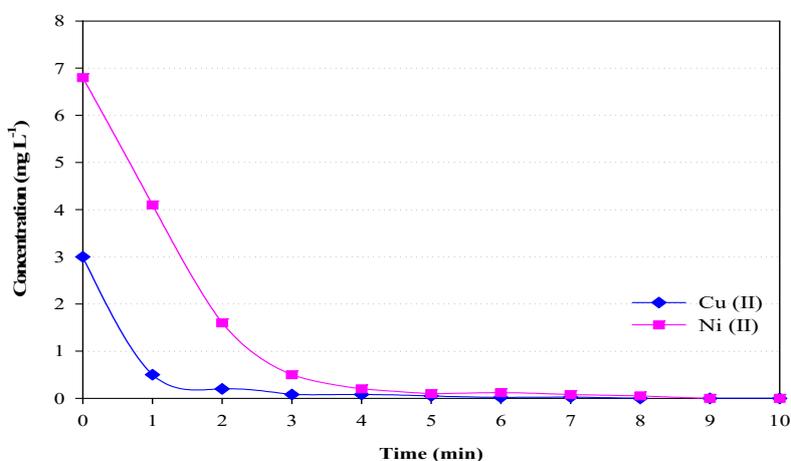


Figure 7. The removal efficiency of Cu and Ni wastewater after EC treatment under the current of  $1.0 \text{ A}$  and  $1.75 \text{ g/L NaCl}$ .

**Table 2.** The comparison table for the EC treatment with previous reports.

Type of Wastewater	Electrode Combination	Optimum Initial pH	EC Time	Optimum Current Density or Current	% Pollutant Removal	Reference
Municipal wastewater	Al-Al	7.4–8.5	20 min	4 mA/cm <sup>2</sup>	90% for COD, 94.56% for turbidity and 49.78% for TDS	Nawarkar, et.al., 2019 [35]
Textile wastewater	Fe-Al	8	80 min-COD, 60 min-Color removal	2 mA/cm <sup>2</sup>	90% COD, 99% for Color removal	Verma, 2017 [36]
Metalworking fluid wastewater	Al-Al, Fe-Fe	6.5 for Al, 7.5 for Fe	25 min	80 A/m <sup>2</sup>	94% COD (Al), 90% COD (Fe), 83% TOC (Al), 80% TOC (Fe)	Demirbas, et.al., (2016) [37]
Olive oil mill wastewater	Ti-Fe	5.2	60 min	39.06, 78.1 and 117.18 A/m <sup>2</sup>	COD and phenolic compounds were 99.89%, 96.14% and 89.97%	Yazdanbakhsh, et.al., (2013) [38]
Printed circuit board (PCB) industrial Wastewater	Al-Graphite	3.0	3–8 min	1.0 A	3 min < (Cu&Ni) 1.0mg/L, 100% removal (8 min)	Present work

#### 4. Conclusions

According to experimental results, several conclusions can be drawn:

- (1) Chloride ions are favored to avoid the passivation of the aluminum anode in the EC system.
- (2) Chloride ions used as the electrolyte can facilitate the release of Al<sup>3+</sup>, which results in the current efficiency of over 100% in the EC system.
- (3) For the wastewater of the PCB (printed circuit board) factory, the EC system could remove Cu<sup>2+</sup> and Ni<sup>2+</sup> effectively (both Cu and Ni concentration of treated wastewater were less than 1.0 mg/L within three minutes).
- (4) The pH value of PCB wastewater could maintain stably about 9.0 in the EC system when the initial pH value was around 2.5.
- (5) The estimated electricity consumption for treating PCB wastewater by the EC process was pertaining to 0.894 kWh for each meter of cubic wastewater.

**Author Contributions:** Conceptualization and methodology—J.-H.C., C.-D.D. and C.-H.H.; formal analysis, investigation and data curation—C.-H.H.; validation, C.-W.C.; writing—original draft preparation—C.-H.H. and S.-Y.S.; writing—review and editing—M.K., B.D. and S.-Y.S.; supervision—J.-H.C. and C.-D.D. All authors have read and agreed to the published version of the manuscript.

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