

## Copper(II), Chromium(VI) and Nickel(II) Removal from Metal Plating Effluent by Electrocoagulation

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The present study is on the removal of Cu(II), Cr(VI), Ni(II) from metal plating wastewater by electrocoagulation (EC) in a batch mode using aluminum (Al), iron (Fe) and stainless steel (St) electrodes. The various parameters like pH (3, 5, 7, 9), current density (30, 70, 90 A/m<sup>2</sup>), electrolyte (NaCl) concentration (800, 1200 mg/L) and operation time of EC (2.5–60 min) on the removal efficiency of metals were studied. The needed operation time of EC to simultaneously provide %100 Cu, %100 Cr and 100% Ni removal at a pH of 2.42 (original) and a current density of 50 A/m<sup>2</sup> was 30 min. For Fe-Fe, Fe-Al pairs, 40 min. for Fe-St, Al-Al, Al-Fe, and 60 min. for Al-St, respectively. By comparing all electrode pairs with each other with respect to desired operating, Fe-St electrode pair was chosen as the optimum for the subsequent of experiments. When only Fe-St pair was used, the removal efficiencies of 100% for all metals were determined at a pH of 9, a current density of 90 A/m<sup>2</sup> and a NaCl addition of 800 mg/L. The characteristics of the sludge produced after 60 min. EC were analysed by X-ray diffractometer (XRD), and SVI values for electrode pairs were calculated. The XRD analysis of the sludge produced during EC revealed that Magnetite(Fe<sub>3</sub>O<sub>4</sub>), Gibbsite(Al(OH)<sub>3</sub>) and Kaolinite(Al<sub>4</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>8</sub>) were the main by-product formed after EC.

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**Keywords:** Cu, Cr, Ni removal, metal plating wastewater, electrocoagulation, EC sludge, X-ray

### 1. INTRODUCTION

Wastewater discharged from metal plating processes contains toxic substances such as cyanides, alkaline cleaning agents, degreasing solvents, oil, fat and toxic metals such as Cd, Cr, Cu, Ni, Zn, Pb have a fatal effect on the human body as well as causing environmental pollution and the indigenous aquatic biota even at low levels, and heavy metal ions are known to be carcinogenic [1,2].

Therefore, the toxic and hazardous effluents that emanate from the metal plating factories must be properly treated so that they do not cause more damage to the environment [3,4].

Various techniques are used for heavy metal removal from industrial wastewaters which include ion-exchange, adsorption, chemical precipitation, membrane filtration, flocculation, coagulation, flotation, reverse osmosis and electrochemical methods [5]. Precipitation is most applicable among these techniques and considered to be the most economical [6]. Although precipitation is shown to be quite efficient in treating industrial effluents, the chemical coagulation may induce secondary pollution caused by added chemical substances [7]. These disadvantages encouraged many studies on the use of EC for the treatment of several industrial effluents [8]. EC is based on creating metallic ions and hydroxide flocks within the water by electrodisolution of the anode usually made of iron or aluminum. The resulting metal ions and hydroxides have the ability to break emulsions and colloidal solution and to remove metal ions and organic pollutants by adsorption [9]. The advantages of EC are high particulate removal efficiency, compact treatment facility, ease of operation, reduced sludge production, and the possibility of complete automation [10,11].

EC technique uses a direct current source between metal electrodes immersed in polluted water. The electrical current causes the dissolution of metal plates including iron or aluminum into wastewater. The metal ions, at an appropriate pH, can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants [12]. In an EC process, the coagulating ions are produced in situ involving three successive stages: (1) formation of coagulants by electrolytic oxidation of sacrificial electrode such as iron or aluminum, (2) destabilization of the contaminants, particulate suspension and breaking of emulsions, (3) aggregation of the destabilized phases to form flocs [3]. Aluminum ( $\text{Al}^{3+}$ ) and iron ( $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ) electrodes are widely used in the EC method. These electrodes generate metal hydroxides such as  $\text{Al}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  by reacting with water, after which treatment begins in the system by coagulation, adsorption and co-precipitation [13]. The reactions in the EC process are as follows [1].

*Aluminum electrode for anode*



*Alkaline conditions*



*Acidic conditions*



*Iron electrode for anode*



*Alkaline conditions*



*Acidic conditions*



*Reactions at cathode*



The electrocoagulation has been successfully used to treat different industrial wastewaters such as, almond industry [14], petroleum refinery wastewater [15], yeast wastewater [16] potato chips wastewater [17], textile wastewater [18], slaughterhouse wastewater [19], dairy wastewater [20], alcohol distillery wastewater [21], olive mill wastewaters [6], chemical mechanical polishing wastewater [22], restaurant Wastewater [23], urban wastewater [24], sanitary landfill leachates [25], yogurt industry wastewater [26], waste metal cutting fluids [27], paper mill wastewater [28], metals in leachate from sewage sludge [29], pesticide [30] and phosphate and nitrogen removal. [31] In addition, a great deal of work performed in the last decades has proved that electrocoagulation is an effective technology for the treatment of heavy metal containing industrial wastewaters. [1,7,32,33]

The main goal of this work was to investigate the effect of type of electrode, pH, current density, and supporting electrolyte on the removal of Cu, Cr, and Ni ions from a metal plating wastewater by EC in a batch reactor in relation to removal efficiency, electrical energy and electrode consumption, and sludge production.

## 2. MATERIAL AND METHODS

### 2.1. Wastewater Characterization

The wastewater used in this study was obtained from Karne Metal Kaplama Sanayi A.Ş. plant with 20 m<sup>3</sup> daily wastewater production capacity located in Fatsa, Turkey. Unicam 929 model atomic absorption spectrophotometer was used for copper, chromium and nickel determination, while pH and conductivity measurements were made with Orion 4 Star model pH and conductivity meter. Chemical and physical properties of the wastewater are given in Table 1. The wastewater was filtered through quartz sand to ensure the removal of suspended particles prior to being used in experiments.

**Table 1.** Characteristics of wastewater used

Characteristics	Value
Cu mg L <sup>-1</sup>	12.6
Cr mg L <sup>-1</sup>	13.9
Ni mg L <sup>-1</sup>	165
pH	2.42
Conductivity mS cm <sup>-1</sup>	2.01

### 2.2. Apparatus and Procedure

For EC experiments, a rectangular Plexiglas reactor with dimensions of 6.45x9.95x11.2 cm was used. All experiments were conducted with 0-60 minute EC times. The reactor was mounted on the center of a magnetic agitator. As the anode and the cathode, six different combinations of Fe, Al and stainless steel (grade 304) with 4.5 cm width x 7.33 cm length x 0.25 cm thickness were used in the experiment. The electrodes were placed in the reactor in monopolar parallel mode and vertical

position, and connected to a direct current power source (GW GPC-3060D DC Power Supply – 30 V, 6 A). In each stage of the experiment, 3 anode and 3 cathode electrodes with 197.91 cm<sup>2</sup> total active anode surface area consisting of the sum of the back and front sides of the electrodes were placed 2.3 cm from the reactor base with 6 mm distance in between. EC experiments were conducted in galvanostatic mode: the current was set and the potential found its own value dependent on the system's overall resistance [34]. In each experiment, the EC reactor was filled with 610 ml wastewater, and agitated continuously at 200 rpm with a cylindrical magnetic bar 2.5 cm long with a diameter of 0.75 cm positioned at the base of the reactor. Through the observation of circular wastewater movements on the surface of the wastewater in the reactor during the agitation, the agitation speed was considered to be adequate, and that the sludge flocs were not disturbed. The electrodes covered with a microfilm layer after each EC experiment were placed in concentrated hydrochloric acid (%37 HCl) for a few minutes and dried at 110 °C for 30 minutes before being used in following experiments. In order to determine the changes in metal ions in the EC cell, 5 ml wastewater samples taken periodically from the EC reactor were filtered through a micro-porous membrane filter with 0.45 µm pores, and acidified in dilution stage with 10% nitric acid, then Cu, Cr and Ni concentrations remaining in wastewater were measured with air acetylene flame atomic absorption spectrophotometer (AAS). Amounts of sludge formed in the reactor after the 60 minute experiment was determined gravimetrically.

### 2.3. EC Sludge Characteristics

A Pyrex glass column with an inner radius of 5.05 cm and height of 33.5 cm was used to determine the sludge amounts formed after a total of 60 minutes of EC, and the SVI values. In the samples prepared from the sludge samples taken by 24 hour dehydration at 110 °C, oxide components were determined using XRD analysis.

### 2.4. Analysis and Calculations

XRD analyses of EC sludge samples was carried out using a PAN Analytical Empyrean diffractometer (2θ range: 0-70, Cu<sub>Kα</sub>: λ=1.54 Å), while metal measurements using a Unicam 929 atomic absorption spectrophotometer (AAS), pH and conductivity measurements using Orion 4 Star pH meter-conductivity meter, turbidity measurements using Jenway 6035 Turbidimeter, and weighing using Sartorius CP224S. For the wastewater, 0.1 or 1 M NaOH and HNO<sub>3</sub> was used for pH adjustments, and necessary amounts of NaCl for conductivity adjustments. All the inorganic chemicals used were analytical grade and all reagents were prepared in Millipore milli-Q deionized water.

Electrical energy consumption was calculated the following equation [35]:

$$E = \frac{U \cdot I \cdot t}{V}$$

where E is the energy consumption (kWh/m<sup>3</sup>), U is the applied voltage (V), I is the current intensity (A), t is the electrocoagulation time (h), and V is the volume of the treated wastewater (L).

### 2.5. Current efficiency

The current efficiency ( $\varphi$ ) was calculated by means of Eq. (1) [36] in optimized conditions.

where  $\varphi$  is the current efficiency (%),  $\Delta M_{\text{exp}}$  is the experimental mass variation and  $\Delta M_{\text{theoretical}}$  is the theoretical mass variation of the electrodes during the EC experiments. The theoretical mass loss can be calculated according to Faraday's law (Equation (2) [37]).

$$\varphi = \frac{\Delta M_{\text{exp}}}{\Delta M_{\text{theoretical}}} 100 \quad (1)$$

$$\Delta M = \frac{I \cdot t \cdot M_w}{z \cdot F \cdot V} \quad (2)$$

where  $\Delta M_{\text{theo}}$  (kg Al or Fe electrode/m<sup>3</sup> treated wastewater) is the theoretical amount of ion produced by current  $i$  (A) passed for a duration of operating time  $t$  (s),  $z$  is the number of electrons involved in the oxidation/reduction reaction; for Fe,  $z_{\text{Fe}} = 2$  and for Al,  $z_{\text{Al}} = 3$ .  $M_w$  is the atomic weight of anode material ( $M_{w,\text{Fe}} = 0.05585$  kg/mol,  $M_{w,\text{Al}} = 0.02698$  kg/mol),  $F$  is the Faraday's constant (96485 C/mol) and  $V$  is the volume (m<sup>3</sup>) of the wastewater in the EC reactor.

### 2.6. SVI

Sludge settleability can be expressed by means of the SVI [38]. SVI is often recommended for characterization of sludge formation, and is defined considering a particular point of the settling curve, namely  $t = 30$  min as follows:

$$\text{SVI}(\text{mL} \cdot \text{g}^{-1}) = \frac{H_{30}}{H_0 \cdot \text{SS}} 1000$$

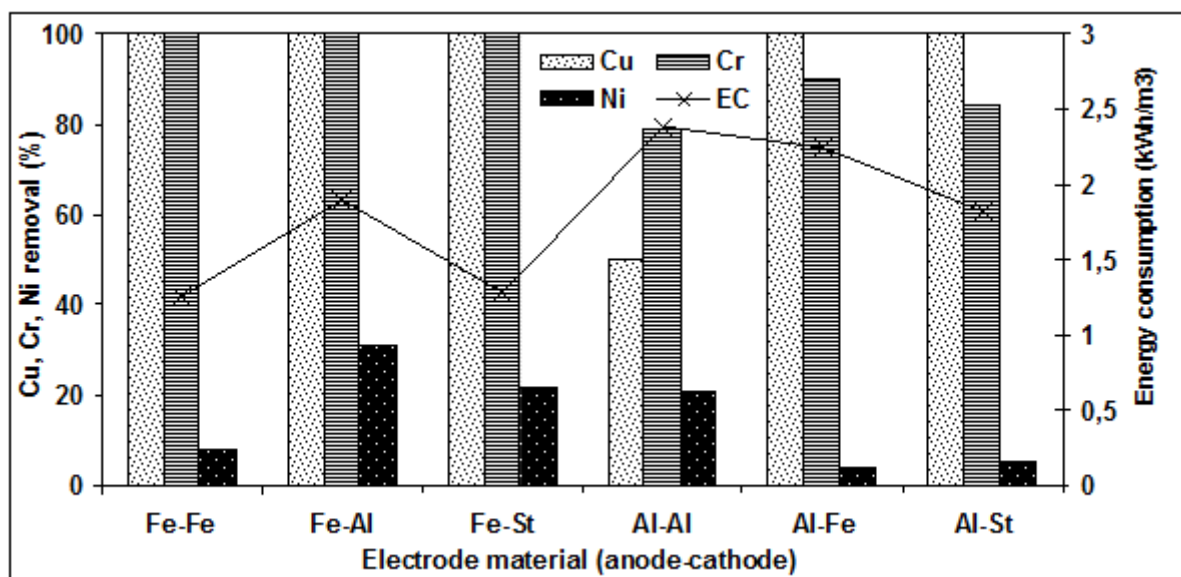
where  $H_{30}$  is the sludge height after 30 min settling (cm),  $H_0$  the initial height of the electrocoagulated waste in the settling column (cm) and  $\text{SS}$  the initial sludge concentration after electrocoagulation treatment ( $\text{g L}^{-1}$ ).

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of Electrode Materials

In order to examine the effect of different electrode pairs on Cu, Cr and Ni removal efficiencies from the metal coating plant wastewater using the EC method, Fe, Al and stainless steel (St) electrode configuration was arranged as Fe-Fe, Fe-Al, Fe-St, Al-Al, Al-Fe, and Al-St electrode pairs. Metal removal efficiencies of electrode pairs and electrical energy consumptions are given in Figure 1, and pH and conductivity changes in the EC reactor, and the amounts of sludge formed, as well as, the calculated SVI values are given in Figure 2. Graphical comparison of electrode pairs was carried out using the data obtained from 10 minutes of EC. As shown in Figure 1, while, after 10 minutes of EC with Fe-Fe, Fe-Al and Fe-St electrode pairs, 100% Cu-Cr removal was achieved with 1.25, 1.90, 1.28

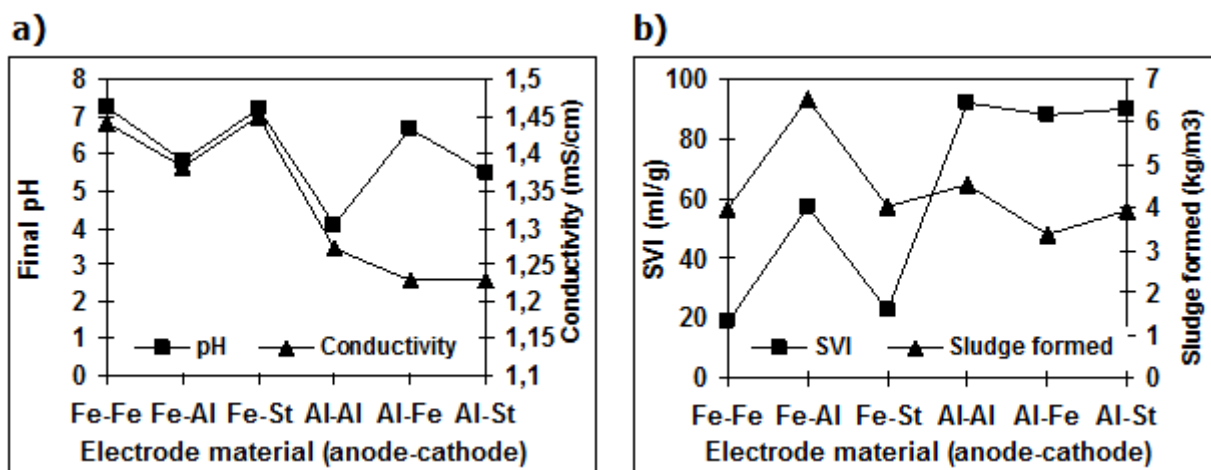
kWh/m<sup>3</sup> energy consumption respectively; Cu-Cr removal efficiencies using Al-Al, Al-Fe and Al-St electrode pairs with 2.38, 2.24, 1.82 kWh/m<sup>3</sup> energy consumption were 50-79%, 100-90%, 100-84% respectively. Ni removal efficiency for Fe-Fe, Fe-Al, Fe-St, Al-Al, Al-Fe and Al-St electrode pairs were 8%, 31%, 22%, 21%, 4% and 5% respectively. For the total EC time of 60 minutes, with the exception of the 98% Cr efficiency using Al-St electrode pair, all metal ions were removed with 100% efficiency with all other electrode pairs at the end of 40 minutes. At the end of this period, electrical energy consumption for Fe-Fe, Fe-Al, Fe-St, Al-Al, Al-Fe and Al-St electrode pairs were 6.42, 11.03, 5.99, 10.28, 11.59 and 10.49 kWh/m<sup>3</sup> respectively. According to Faraday's Law given above with equation 2, anode amounts consumed for Fe and Al electrodes at the end of 40 minutes of EC were 1.11 and 0.35 kg/m<sup>3</sup> respectively. 100% Ni removal efficiencies were obtained using Fe-Fe, Fe-Al, Al-Al and Al-St electrode pairs with 30 minutes of EC, and using Fe-St and Al-Fe electrode pairs with 40 minutes of EC with electrical energy consumption of 4.41, 6.98, 7.63, 7.22, 5.99 and 11.59 kWh/m<sup>3</sup> respectively.



**Figure 1.** The effect of different anode-cathode pairs on metal removal efficiency and energy consumption (EC time: 10 minutes, current density: 50 A/m<sup>2</sup>, initial pH: 2,42, initial conductivity: 2,01 mS/cm)

pH and conductivity changes after 10 minutes of EC are given in Figure 2a, while amounts of sludge formed after 60 minutes of EC and calculated SVI values are given in Figure 2b. In most cases, the solution pH increased as electrocoagulation progressed because of continuous OH<sup>-</sup> formation at the cathode as shown by eq 7 [1]. As seen in Figure 2a, the initial wastewater pH value of 2.42, for Fe-Fe, Fe-Al, Fe-St, Al-Al, Al-Fe and Al-St, increased to 7.25, 5.79, 7.18, 4.1, 6.66 and 5.50 respectively at the end of 10 minutes of EC. The highest increase in pH was obtained with Fe-Fe and Fe-St electrode pairs respectively.

Similarly, wastewater initial conductivity value of 2.01 mS/cm decreased to 1.38, 1.44, 0.96, 0.98 and 0.95 mS/cm respectively using the same electrode pairs.



**Figure 2.** The effect of different anode-cathode pairs on a)SVI and sludge formed, b)final pH and conductivity (EC time: 10 minutes, current density: 50 A/m<sup>2</sup>, initial pH: 2.42, initial conductivity: 2.01 mS/cm)

Figure 2b shows the sludge production amounts represented as suspended solid materials after 60 minutes of EC, and SVI changes. When sludge amounts for Fe-Fe, Fe-Al, Fe-St, Al-Al, Al-Fe and Al-St electrode pairs were 3.98, 6.55, 4.03, 4.55, 3.33 and 3.94 kg/m<sup>3</sup> respectively, the corresponding sludge volume index values were calculated to be 18.93, 57.07, 22.45, 92.24, 88.30 and 89.98 ml/g respectively. These values being lower than 100 ml/g indicate that the sludge obtained using every electrode pair show good precipitation characteristics. [39] The lowest SVI values were obtained with Fe-Fe, followed by Fe-St electrode pairs. When iron was used as the anode, the formation of iron particles resulting in a brown colored turbidity was observed. Electrode pairs forming coloration, from the highest to the least, were determined to be Fe-St, Fe-Fe and Fe-Al. Chen et al. [10] in his study on the treatment of restaurant wastewater with EC, very similar to the results of this study, determined that treated water was very clear and stable when Al electrode was used, while it was initially greenish, then yellowish and turbid when Fe electrode was used. After 60 minutes of EC, the turbidity of the wastewater for Fe-Fe, Fe-Al, Fe-St, Al-Al, Al-Fe and Al-SS anode-cathode pairs was measured to be 10.54, 4.10, 9.77, 0.03, 7.80 and 0.00 NTU respectively. In electrode pairs using St as the cathode, much smaller gas bubbles were observed in the froth forming on the surface of the EC reactor. Formation of thick gel-like flocs in the reactor with aluminum anodes and cathodes, and for samples taken for metal analysis, relatively slow filtration rates through 0.45 μm micro-porous membrane filter was observed. In EC time periods, minimum energy consumption occurred with the Fe-St pair, and maximum sludge production took place with the Fe-Al pair. Anode consumption for 10-60 minute EC times where Fe and Al was used as anodes varied between 0.27-1.67 and 0.08-0.53 kg/m<sup>3</sup> respectively according to Faraday's Law. For the comparison of experimental and theoretical anode consumptions, using the theoretical (Equation 2) and experimental anode consumptions at the end of 60 minutes of

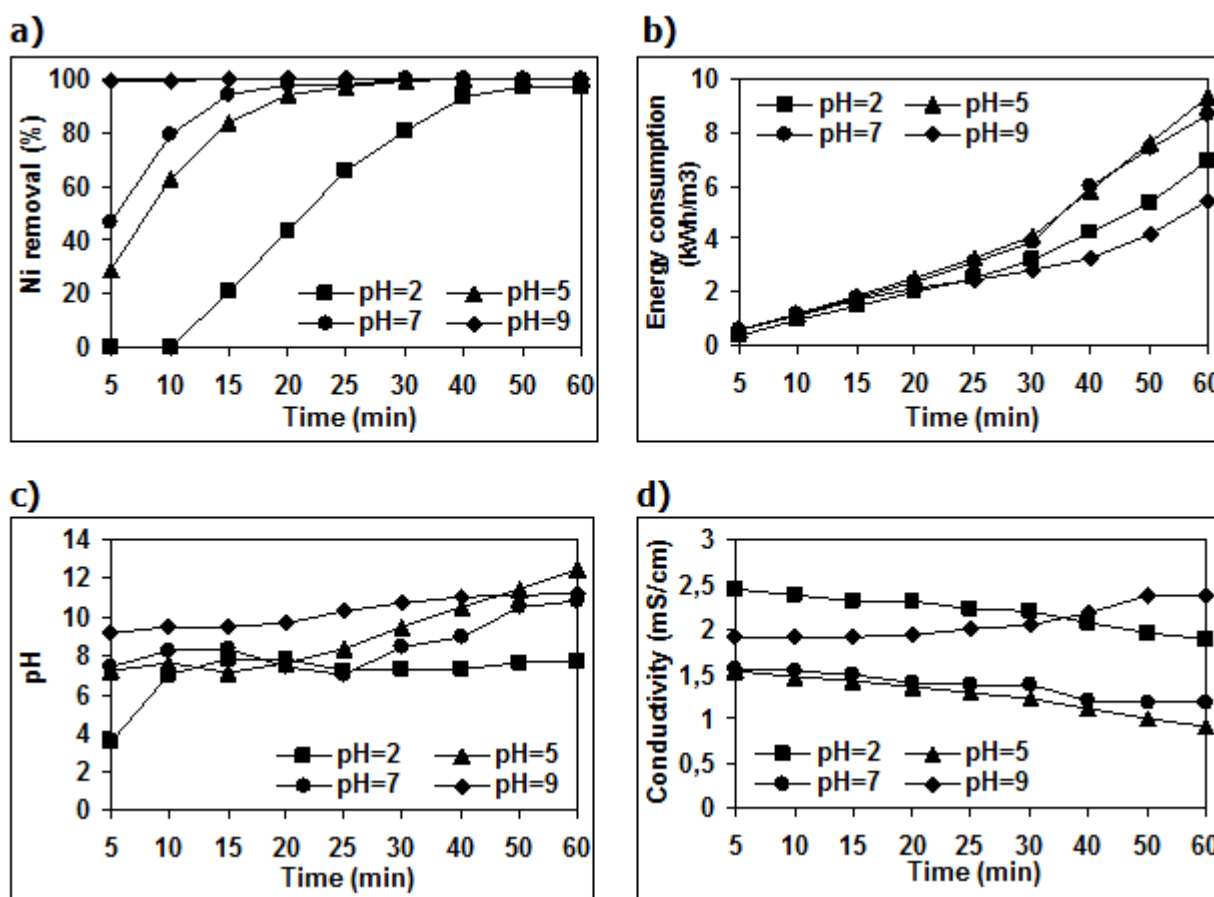
EC determined for Fe-Fe and Fe-St electrode pairs, current efficiencies for Fe-Fe and Fe-St electrode pairs were calculated to be 101.6% and 105.6% respectively. According to Kim et al. [40], current efficiency increases with surface area of the electrode. In this study where all electrode pairs had equal anode surface areas, the high current efficiency values could be explained by the dissolution resulting from the corrosion of anode surfaces originating from the low wastewater pH during early EC times and high conductivity [41]. It was concluded that the EC sludges of Fe anodes were much more compact than those of Al anodes, and that St should be used as the cathode in the following stages of this study as it is an inert electrode. Using Fe as the anode, higher metal removal and current efficiencies, lower energy consumptions, as well as, lower sludge volume indices were obtained when compared to Al. The superiority of Fe to Al would be due to the higher adsorption capacity of heavy metals by hydrous ferric oxide than hydrous aluminum oxide [42]. On the other hand, in some studies on metal removal from industrial wastewater using EC, higher efficiencies were reached with Al electrodes than with Fe electrodes [32]. This indicates that anode-cathode pairs could yield different results depending on the characteristics of the wastewater. In the following stages, the experiments were conducted using the Fe-St electrode pair.

### 3.2. Effect of Wastewater pH

The initial pH is of vital importance in the performance of many electrochemical processes and chemical coagulation operations [43,44]. Otherwise, when conductivity is high, pH effect is not significant [45]. Hydrated  $\text{Cr}(\text{OH})_3$  has minimum solubility at pH 8.5 [43]. According to the Cu-Pourbaix diagram, copper is solid in the form of  $\text{Cu}(\text{OH})_2$  at pH approximately  $>4.5$  until pH 14. Nickel is also solid in  $\text{Ni}(\text{OH})_2$  form at pH approximately  $>6$  according to its Pourbaix diagram [46]. Using an Fe-St electrode pair, the effect of pH on Cu, Cr and Ni removal was inspected for pH values of 2-5-7-9 at  $50 \text{ A/m}^2$  for 5-60 minute EC time. Initial conductivity values of wastewater with a conductivity of  $2.01 \text{ mS/cm}$  were measured at 2.49, 1.57, 1.63 and  $1.65 \text{ mS/cm}$  for pH values of 2-5-7-9 respectively. Only Ni removal efficiencies were graphically represented (Figure 3a) as after 5 minutes of EC, 42% and 48% Cu and Cr removal efficiencies were reached together with  $0.37 \text{ kWh/m}^3$  energy consumption and  $0.13 \text{ kg/m}^3$  anode consumption at pH 2, while 100% Cu and Cr removal efficiencies were reached for pH 5, 7 and 9 with respectively  $0.60$ ,  $0.58$  and  $0.57 \text{ kWh/m}^3$  energy consumptions, and  $0.13 \text{ kg/m}^3$  anode consumption for each pH value. In their EC study of synthetic wastewater containing  $800 \text{ mg/L}$  Cr, Cu and Zn, Adhoum et al. [6] identified a decrease in Cr removal efficiencies at pH values higher than 8 at  $160 \text{ A/m}^2$  current density. However, a decrease was not observed at high pH values in this study as the wastewater used contained low concentrations of Cr ions. According to Figure 3a-b, for 100% removal values, pH 5, 7 and 9, and after 40, 30 and 15 minutes of EC, respectively  $5.78$ ,  $3.85$  and  $1.72 \text{ kWh/m}^3$  energy consumptions (Figure 3b) and  $1.11$ ,  $0.83$  and  $0.41 \text{ kg/m}^3$  anode consumptions were calculated. It was determined that efficiency increased with pH, and anode consumptions decreased with energy consumptions. In their study on EC in industrial wastewater using Al and Fe electrodes, Kim et al. [47] determined that copper removal efficiencies increased with pH. Similar results were obtained by Al-Aji et al. [46] on removal of Cu,



Ni, Mn and Ni from synthetic wastewater using EC. In experiments conducted at 50 A/m<sup>2</sup> current density and with original wastewater (pH=2.42), the energy consumption at which all metal ions were removed with 100% efficiency after 40 minutes of EC was 5.99 kWh/m<sup>3</sup>. However, in subsequent experiments where the effect of current density was studied, 100% removal efficiency for all metal ions was reached after 50 minutes of EC at 30 A/m<sup>2</sup> current density and with 2.98 kWh/m<sup>3</sup> energy consumption. This result indicates that metal ions in wastewater could be treated with 100% efficiency after longer but reasonable EC times by decreasing current densities, and therefore energy consumptions, without the need for pH adjustment. Maximum Ni removal efficiencies for pH 2 reached a maximum of 97% after 50 minutes of EC with 5.35 kWh/m<sup>3</sup> energy and 1.39 kg/m<sup>3</sup> anode consumptions, and did not increase with time. After 20 minutes of EC, a very small difference was determined between the removal efficiencies at pH 5, 7 and 9, and the difference between the effects of pH 2 and other pH values on Ni removal efficiency after 40 minutes of EC was not significant. High efficiency removal of metal ions at high pH values could be explained by the precipitation of hydroxide forms on cathode surfaces. On the other hand, the oxidation of Fe(II) to Fe(III) is adversely affected when Fe is used as the anode and wastewater pH is acidic [48].



**Figure 3.** The effect of initial wastewater pH on a)Ni removal, b)energy consumption, c)final pH, d)final conductivity (current density: 50 A/m<sup>2</sup>, conductivity: 2.49, 1.57, 1.63 and 1.65 mS/cm for pH 2, 5, 7 and 9)

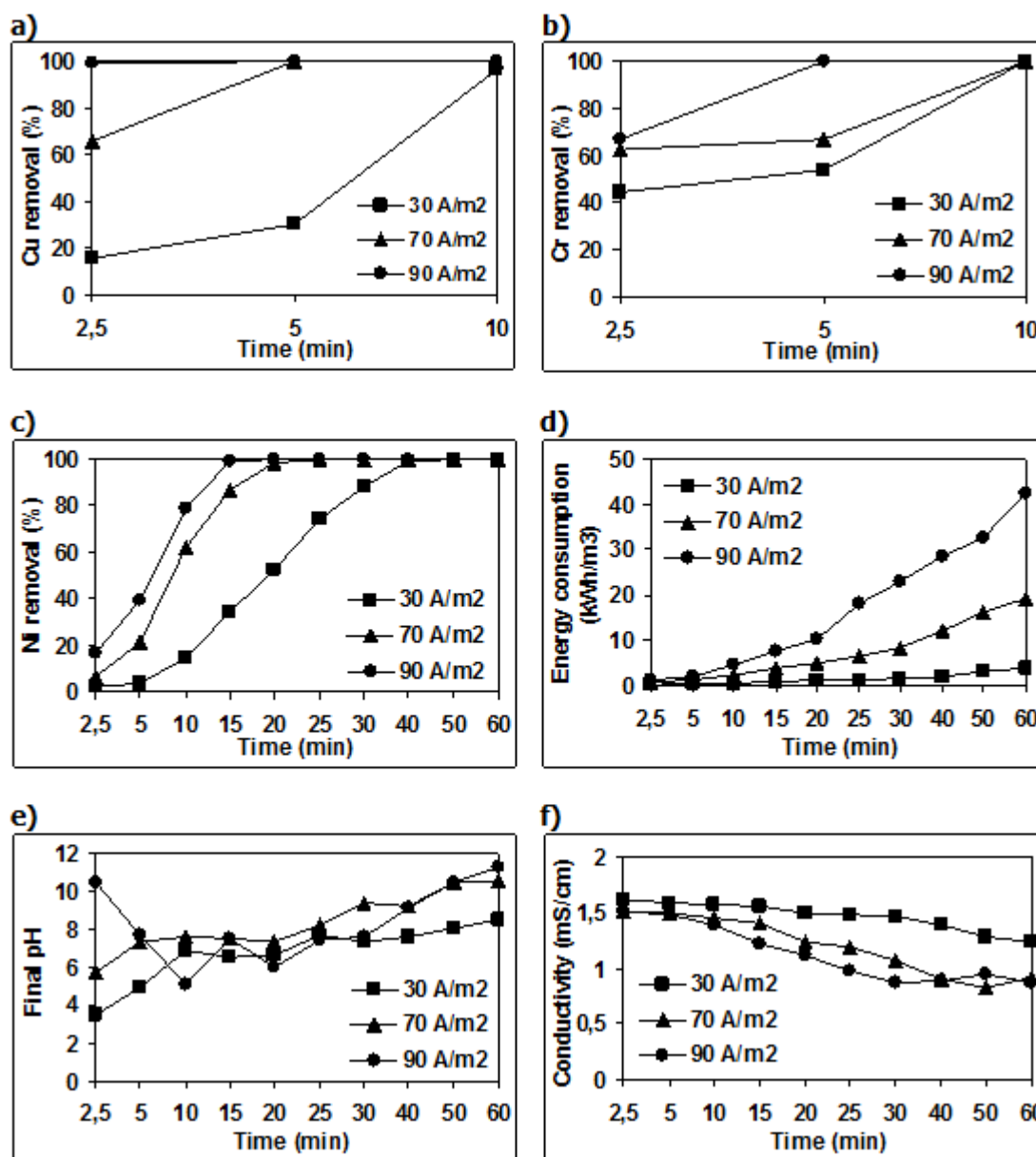
Figure 3c-d shows final pH and conductivity changes respectively. For wastewater initial pH values of 2, 5, 7 and 9, final pH and conductivity values varied between 3.47-7.74, 7.21-12.5, 7.45-10.85, 9.12-11.2 and 2.44-1.88, 1.52-0.92, 1.55-1.17, 1.92-2.37 respectively. At initial wastewater pH value of 2, increases in final pH values was less than other initial pH values due to the buffering effect occurring in the wastewater. At wastewater input pH value of 9, conductivity showed an unexpected increase with time. This condition indicates that flocs are re-ionized resulting in increased conductivity.

Sludge amounts formed after 60 minutes of EC was 3.47, 3.37, 3.33 and 3.15 kg/m<sup>3</sup> respectively for pH 2, 5, 7 and 9. Turbidity values of the wastewater left to precipitate under the same conditions and at the same pH values were measured to be 1.14, 3.95, 2.67 and 1.44 NTU respectively for pH values from 2 to 9.

### 3.3. Effect of Current Density

The current density is the amount of current per area of the electrode. [43] Current density is important parameter for controlling the reaction rate in the EC process. Current density not only determines the coagulant dosage rate but also the bubble production rate and flocs growth which can affect treatment efficiency of the process since the current density increases and the efficiency of ion production on the anode and cathode increases according to Faraday's law [3, 6, 11]. Using Fe-St electrode pair, the effect of current density on Cu, Cr and Ni removal was examined for 2.5-60 minute EC times at 30, 70, 90 A/m<sup>2</sup> current densities. Changes with time in Cu, Cr and Ni removal efficiencies and electrical energy consumption, final pH and consumption values at various current densities is given in Figure 4. Ions dissolved from the anode increase with the current density according to Faraday's Law. When sufficient current was passed through the solution, the dissolved metal ions were hydrolysed and metallic hydroxide species were formed. Thus, the production of floc increased by resulting in an increase in the removal efficiency [26]. Increases in current density result in increases in metal removal efficiency but also increases in energy and electrode consumption; hence the EC process requires an optimal current density for different heavy metal concentrations [47]. Cu, Cr and Ni removal efficiencies varied between 15.83-44.88-2.36%, 65.83-62.70-6.52% and 99.24-67.20-16.90% respectively after 2.5 minutes of EC and at 30, 70, 90 A/m<sup>2</sup> current densities. 100% Cu removal was achieved after 15, 5 and 5 minutes of EC, while 100% Cr removal was achieved after 15, 10 and 5 minutes of EC, and 100% Ni removal was achieved after 50, 25 and 20 minutes of EC at 30, 70 and 90 A/m<sup>2</sup> current densities (Figure 4a-b-c) with 2.98, 6.50 and 10.15 kWh/m<sup>3</sup> electrical energy (Figure 4d) and 0.83, 0.98 and 1.00 kg/m<sup>3</sup> anode consumptions. When current density was raised from 30 A/m<sup>2</sup> to 70 and 90 A/m<sup>2</sup>, electrical energy consumption after EC times in which each metal ion was removed at the same time with 100% efficiency increased 2.18 and 3.40 times respectively, whereas very small changes occurred in anode consumptions. In other words, while each metal ion was removed with 100% efficiency after 50 minutes of EC at 30 A/m<sup>2</sup> current density, EC times in which 100% efficiencies were reached at 70 and 90 A/m<sup>2</sup> current densities decreased to 25 and 20 minutes respectively. Furthermore, the formation of a microfilm layer with sufficient thickness to be

perceptible without any measurements was observed on anode and cathode surfaces at 70 and 90 A/m<sup>2</sup> current densities; which means the current density will increase with time under galvanostatic conditions resulting in a bigger voltage difference.



**Figure 4.** The effect of current density on a-b-c)Cu, Cr and Ni removal, d)energy consumption, c)final pH, d)final conductivity (pH:2.42, conductivity:2,01 mS/cm).

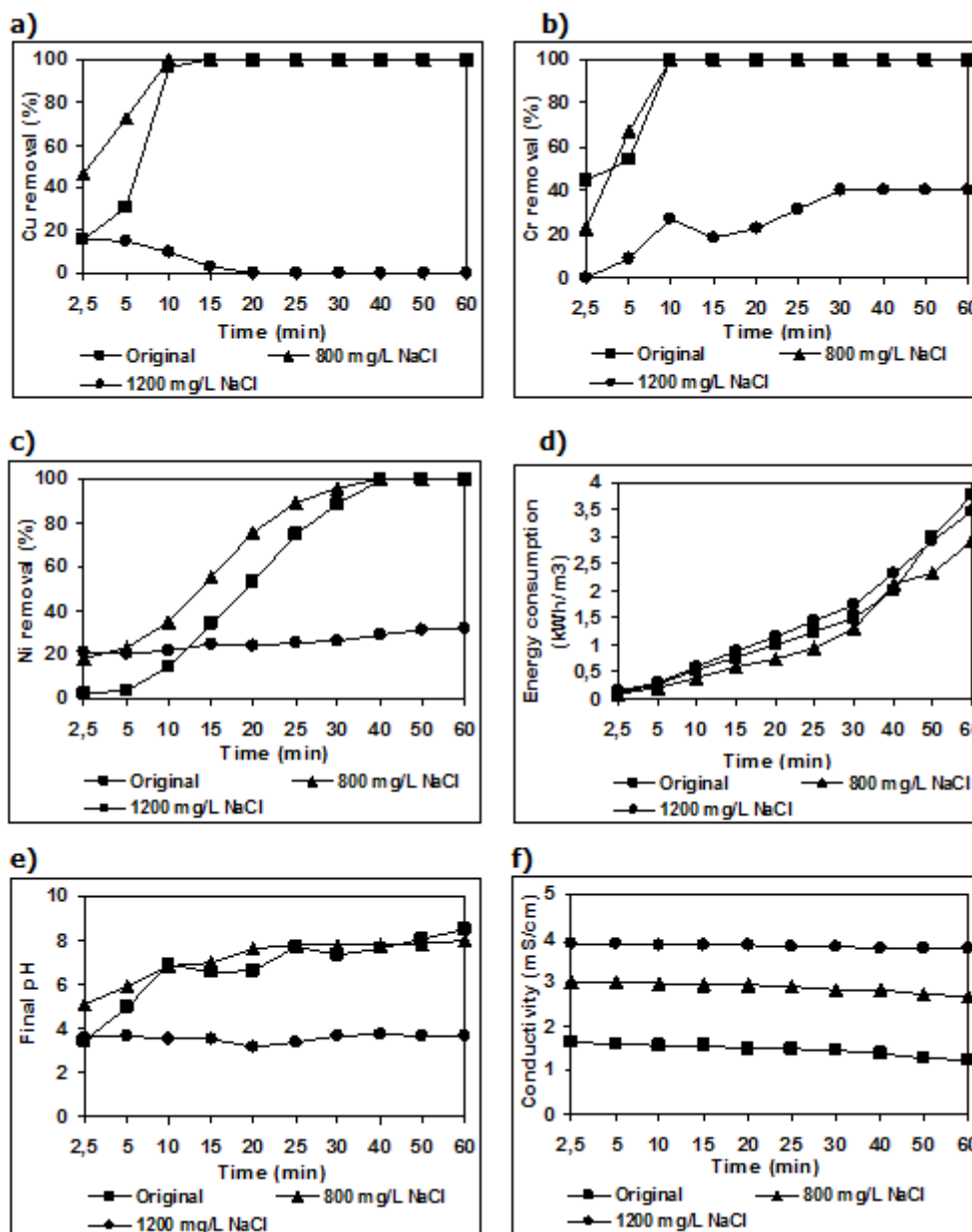
Figure 4e-f shows the changes with time in final pH and conductivity values respectively. At 30, 70 and 90 A/m<sup>2</sup> current densities, final pH values varied between 3.46-8.52, 5.71-10.5 and 10.52-11.25, while final conductivity values varied between 1618-1233, 1.51-0.92 and 1.51-0.86 respectively. As seen in Figure 4e-f, a rapid increase in final pH values and a rapid decrease in conductivity values were identified as the current density increased. The pH increased from the initial

value of 2.42 to respectively 3.46, 5.71 and 10.52 at 30, 70 and 90 A/m<sup>2</sup> current densities after 2.5 minutes of EC.

Amounts of sludge formed after 60 minutes of EC at 30, 70 and 90 A/m<sup>2</sup> current densities were 1.84, 4.20 and 11.10 kg/m<sup>3</sup> respectively. Turbidity values of wastewater left to precipitate for 30 minutes under the same conditions and at the same pH values were measured to be 7.38, 3.35 and 4.95 NTU at 30, 70 and 90 A/m<sup>2</sup> current densities.

### 3.4. Effect of Electrolyte

The conductivity of the wastewater should be sufficiently high in order to reduce the cell voltage and, consequently, the energy consumption [26]. Using Fe-St electrode pair, the effect of NaCl on Cu, Cr and Ni removal was examined with 2.5-60 minute EC times at 30 A/m<sup>2</sup> current density by adding 800 ve 1200 mg/L NaCl to the wastewater. When the conductivity of solution increases, IR-drop decreases, so the necessary voltage to reach on optimum current density will be diminished, and consequently the consumed electrical energy is decreased [4]. The presence of electrolyte in solution during electrolysis is essential to decrease IR drop within the cell and consequently decreases energy consumption. Sodium chloride is commonly employed as an electrolyte in electrocoagulation process for many reasons (i) decrease energy consumption (ii) Cl<sup>-</sup> ions act as antipassive agents and destroy passive layer formed on anode during electrolysis especially in case of Al anode [9]. Figure 5a-b-c shows the effect of NaCl on respectively Cu, Cr and Ni removal, and Figure 5d-e-f shows the changes in electrical energy consumption, final pH and conductivity values with time. The addition of 800 mg/L NaCl has increased the initial conductivity value of 2.01 mS/cm of the wastewater to 3.02 mS/cm. As seen is Figure 5a-b-c, while 100% Cu, Cr and Ni removal efficiencies were reached after respectively 15, 10 and 50 minute EC times at 30 A/m<sup>2</sup> current density without using NaCl, the EC times for 100% removal efficiencies were 10, 10 and 40 minutes with an 800 mg/L NaCl addition. With EC times in which each metal can be removed 100% at the same time, the electrical energy consumed decreased to 2.12 kWh/m<sup>3</sup> from 2.98 kWh/m<sup>3</sup>, and anode consumptions to 0.67 kg/m<sup>3</sup> from 0.83 kg/m<sup>3</sup> when NaCl was added to the wastewater. However, as can be seen from the same figure, an addition of 1200 mg/L NaCl resulted in decreased removal efficiencies for Cu, Cr and Ni. For example, very low efficiencies such as 40, 43 and 31.68% respectively was reached only for Cr and Ni after 60 minutes of EC. Very small changes occurred in wastewater conductivity, pH, and reactor voltage. This condition might be explained by the fact that the oxidation of Fe(II) ions into Fe(III) ions will be prevented in the presence of high concentrations of NaCl, and that the formation of iron oxide flocs and, therefore, removal efficiencies will decrease [49]. It was concluded that the addition of NaCl to wastewater with relatively high conductivity with the purpose of raising the conductivity was not necessary, at least in this particular study, to improve the efficiency and other operating conditions. However, for wastewater with lower initial conductivity values, the electrolyte effect could result in higher efficiencies and shorter EC times.

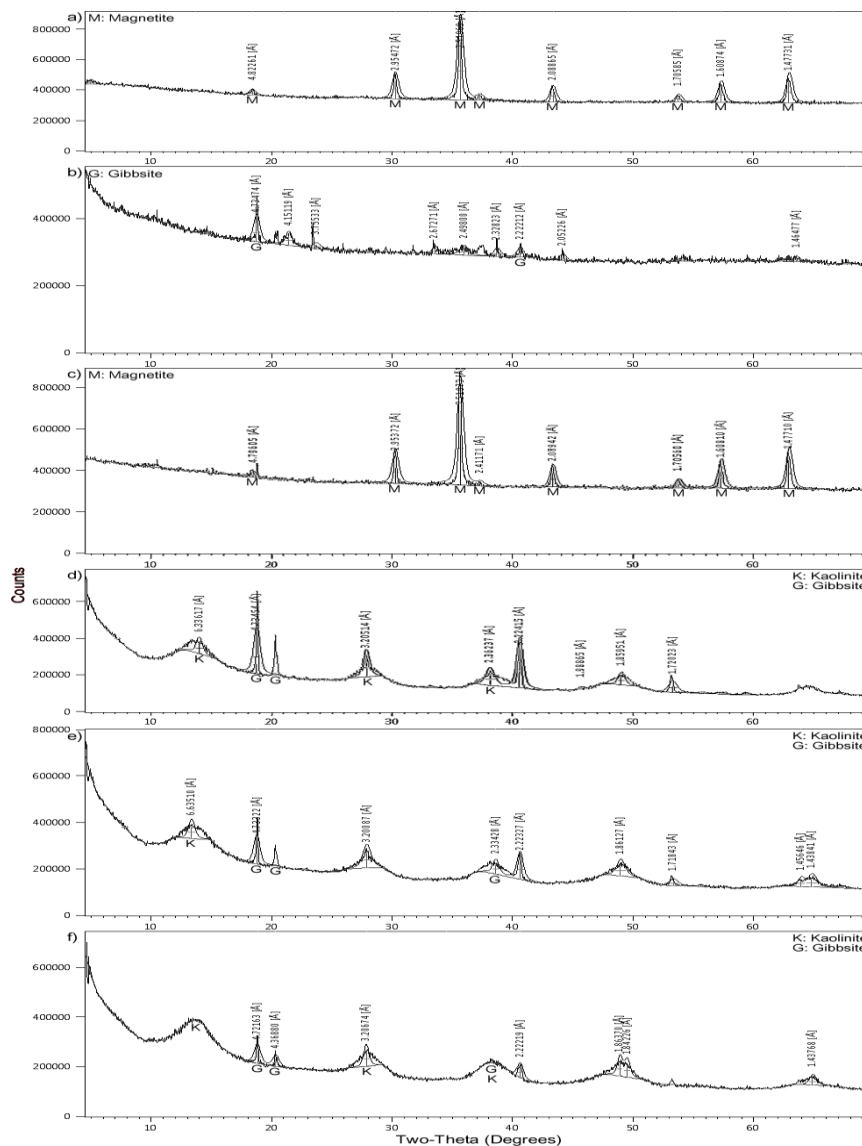


**Figure 5.** The effect of electrolyte (NaCl) addition on a-b-c)Cu, Cr and Ni removal, d)energy consumption, e)final pH, f)final conductivity (current density: 30 A/m<sup>2</sup>, pH: 2.42, conductivity: 3.14 and 4.02 mS/cm with 800 and 1200 mg/L NaCl addition).

As given in Figure 5e-f, final pH values varied between 3.46-8.52, 5.08-7.99 and 3.57-3.68 respectively, and final conductivity values between 1.61-1.23, 3.02-2.67 ve 3.87-3.77 respectively for original wastewater, and wastewater with additions of 800 and 1200 mg/L NaCl with 60 minute EC times. Amounts of sludge formed after 60 minutes of EC was 1.84, 1.55 ve 0.14 kg/m<sup>3</sup> respectively for original wastewater, and wastewater with additions of 800 and 1200 mg/L NaCl. Turbidity values of wastewater left to precipitate for 30 minutes under the same conditions and at the same pH values were measured to be 7.38, 3.78 and 1.93 NTU for original wastewater, and wastewater with additions of 800 and 1200 mg/L NaCl.

## 3.5. XRD Analysis of the Sludge formed during EC

XRD analyses and XRD conditions were given of the sludge formed after EC with 6 different electrode pairs were given in Figure 6. XRD analyses show the EC sludges to have characteristic peaks for mainly magnetite, gibbsite and kaolinite components.



**Figure 6.** XRD conditions of EC sludges of electrode pairs a)Fe-Fe, b)Fe-Al, c)Fe-St, d)Al-Al, e)Al-Fe, f)Al-St; Magnetite:  $\text{Fe}_3\text{O}_4$ ; Gibbsite:  $\text{Al}(\text{OH})_3$ ; Kaolinite:  $\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$ .

## 4. CONCLUSIONS

- After 40 minutes, with the exception of 98% Cr efficiency using Al-St electrode pair, all metal ions were removed with 100% efficiency using all other electrode pairs. Energy consumptions for Fe-Fe, Fe-Al, Fe-St, Al-Al, Al-Fe and Al-St electrode pairs at the end of this period was calculated to be 6.42, 11.03, 5.99, 10.28, 11.59 and 10.49  $\text{kWh/m}^3$  respectively.

- The lowest SVI value was obtained using the Fe-Fe pair (18.93 ml/g), whereas the highest was obtained with the Al-Al electrode pair (92.24 ml/g).
- Metal removal efficiencies increased with the pH and current densities in every stage of the experiment.
- Noticeably thick microfilm layers were observed on the anode and the cathode especially at 70 and 90 A/m<sup>2</sup> current densities; which means the current density will increase with time under galvanostatic conditions resulting in a bigger voltage difference. High currents should be avoided as it will result in an increased electrical resistance in the EC reactor, leading to high electrical energy consumption.
- Electrical energy consumptions were respectively 2.98, 16.21 and 10.15 kWh/m<sup>3</sup> for 100% Cu, Cr and Ni removal efficiencies at the natural pH of the wastewater and 30, 70 and 90 A/m<sup>2</sup> current densities.
- At pH=7 and pH=9, precipitation interphases observed in glass columns quick became apparent in the initial precipitation time of 5 minutes, and the hydroxide flocs formed were bigger than those observed in the wastewater with other initial pH values.
- Significant changes in EC times and metal removal efficiencies were not observed when 800 and 1200 mg/L NaCl was added to the wastewater with an initial conductivity value of 2.01 mS/cm
- The existence of Kaolinite (Al<sub>4</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>8</sub>) and Gibbsite (Al(OH)<sub>3</sub>) in the EC sludges of Al-Al, Al-Fe and Al-St electrode pairs, Magnetite (Fe<sub>3</sub>O<sub>4</sub>) in the EC sludges of Fe-Fe and Fe-St electrode pairs, and Gibbsite in the EC sludge of Fe-Al electrode pair was identified through XRD analyses.

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