Removal of nickel, copper, zinc and chromium from synthetic and industrial wastewater by electrocoagulation

Konstantinos Dermentzis ¹, Achilleas Christoforidis ², Evgenia Valsamidou ²
1- Department of Engineering Science, Laboratory of Chemical Technology and Electrochemistry, Technological Education Institute TEI of Kavala, 65404 Agios Loucas, Kavala, Greece
2- Department of Petroleum Technology, Laboratory of Environmental Protection, Technological Education Institute TEI of Environmental Protection, Kavala
demerz@otenet.gr
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ABSTRACT

In this work, the performance of electrocoagulation with aluminum electrodes for simultaneous removal of nickel, copper, zinc and chromium from synthetic aqueous aliquot solutions and actual electroplating wastewater was studied. Parameters affecting the electrocoagulation process, such as initial pH, current density, initial metal ion concentration, COD and contact time were investigated. Best removal capacity for all studied metals was achieved in the pH range 4-8. Mixed solutions containing the same concentrations of all metals i.e. 75, 150 and 300 mg/L were tested. Nickel, copper and zinc showed similar removal rates. They were completely removed in 20, 40 and 50 minutes respectively, while for the corresponding complete removal of chromium 40, 60 and 80 minutes were needed. Increased current density accelerated the electrocoagulation process, however, on cost of higher energy consumption. Results revealed that best removal was achieved at a current density of 40 mA/cm². The electrocoagulation process was successfully applied to the treatment of an electroplating wastewater sample, where the concentrations of nickel, copper, zinc, chromium and COD were effectively reduced under the admissible limits in 60 minutes. Consequently, the electrocoagulation process is a reliable, safe and cost-effective method for removing heavy metals and COD from water and wastewater.

Key words: Electroplating wastewater; electrochemical coagulation; heavy metal Removal, aluminum anode

1. Introduction

Industrial effluents from electroplating industries contain high amounts of heavy metal ions, such as chromium, nickel, copper, cadmium and zinc. These heavy metal bearing wastewaters are of considerable concern because they are non-biodegradable, highly toxic and probably carcinogenic. Only 30-40% of all metals used in plating processes are effectively utilized i.e. plated on the articles. The rest contaminates the rinse waters during the plating process when the plated objects are rinsed upon removal from the plating bath. Electroplating rinse waters may contain up to 1000 mg/L toxic heavy metals which, according to environmental regulations worldwide must be controlled to an acceptable level before being discharged to the environment. Several treatment processes have been suggested for the removal of heavy metals from aqueous waste streams: adsorption (Lazaridis et al., 2005), biosorption (Senthikumar et al., 2010), ion exchange (Inglezakis et al., 2003), chemical precipitation (Kurniawan et al., 2006) and electrochemical methods: electrowinning (Bolger
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& Szlag, 2004), electrodialysis (Marder et al., 2004), electrodeionization (Yeon et al., 2003; Lu et al., 2010), membrane-less electrostatic shielding electrodialysis/electrodeionization (Dermentzis, 2010; Dermentzis et al., 2010) and electrocoagulation. Chemical hydroxide precipitation is the most economic and the most commonly utilized procedure for the treatment of heavy metal-bearing industrial effluents but after this treatment the wastewater stream can still contain up to 5 ppm heavy metals (Kurniawan et al., 2006), which is an unacceptable concentration for discharge to the environment. In order to remove heavy metals down to the ppb concentration level, the wastewater stream must be further treated using a second sulfide precipitation as a polishing step or a series of ion exchange columns. The large amounts of the precipitated sludge containing the concentrated heavy metal hydroxides or sulfides is an extremely hazardous waste and must be disposed of using special facilities at great expense to industry. From the viewpoint of environmental protection and resource saving, effective recycling and reusing of the heavy metal wastewater is strongly expected. Closed-recycle system or so-called effluent-free technology should be developed. Chemical coagulation is a quite effective method for treating heavy metal bearing wastewaters but may induce secondary pollution by adding coagulants, such as aluminum or iron salts or organic poly-electrolytes to remove colloidal matter as gelatinous hydroxides. Also this wastewater treatment process produces large amounts of sludge.

Electrocoagulation uses no chemicals as coagulating agents. These are generated during the electrolysis process by electro-dissolution of a sacrificial anode made of aluminum or iron. Electrocoagulation has been successfully performed for decolorization treatment of dyes and remediation of dye-house wastewaters (Kobya et al., 2003; Akbal and Kuleyin, 2010), treatment of oil wastes (Adhoum and Monser 2004; Un et al., 2009), diary effluents (Tchamango et al., 2010), diesel and bio-diesel wastewaters (Chavalparit and Ongwande, 2009; El-Naas et al., 2009), laundry wastewaters (Wang et al., 2009), slaughter house effluents (Asselin et al., 2008), arsenic or fluoride containing waters (Hansen et al., 2007; Hu et al., 2008) and heavy metal bearing effluents (Kongsricharoern and Polprasert, 1996; Adhoum et al., 2004; Heidmann and Calmano 2008; Nouri et al., 2010).

This paper reports the efficiency of electrocoagulation in removing metallic pollutants, such as nickel, copper, zinc and chromium from synthetic aqueous solutions and actual wastewater obtained from a local electroplating unit.

2. Materials and Methods

2.1 Chemicals

KCl, NiSO$_4$$\cdot$7H$_2$O, CuSO$_4$$\cdot$5H$_2$O, ZnSO$_4$$\cdot$7H$_2$O, K$_2$Cr$_2$O$_7$ and NaOH were of analytical grade (Merck). pH was adjusted by 0.1 M solutions of HCl and NaOH as required. The actual wastewater was obtained from an electroplating unit located near Thessaloniki, northern Greece.

2.2 Apparatus

A laboratory model DC power supply apparatus (PHYWE Systeme GmbH & Co. KG. Germany) was used to maintain constant DC current. Voltage and current were measured by a multimeter (PHYWE). Conductivity was measured by means of a conductometer (inoLab Cond. Level 1, WTW). The pH and the temperature were measured using a Hanna (HI8314) pH-meter connected to a combined electrode comprising a temperature sensor (HI1217D).
The chemical oxygen demand (COD) was analyzed using a COD reactor (Thermoreaktor TR 420, MERCK) and a direct reading spectrophotometer (Spectroquant Pharo100, MERCK). Electrolyses were conducted at room temperature in a cylindrical glass cell of 400 ml in which aliquot solutions of 250 ml were placed and slowly stirred with a magnetic bar at 500 rpm. A pair of commercially obtained aluminum plates of size 10 cm x 5 cm x 0.5 cm immersed to a 6 cm depth with an effective area of 30 cm$^2$ each, were used as electrodes in the experiments. The inter-electrode distance was 1.5 cm. To remove the oxide and passivation layer from aluminium surface the electrodes were grinded with sandpaper and energized by dipping them in 5N HCl for 1 minute. 0.5 g KCl was added to every treated solution. The added KCl serves for prevention of passivation on the aluminium electrode surface and decrease of the excessive ohmic drop in the solution. The polarity of the cell was reversed every 30 minutes to limit the formation of the passivation layers on the electrodes. Samples were extracted every 10 minutes and filtered using Whatman filter paper (Grade 40). The residual heavy metals concentrations were determined by Atomic Absorption Spectroscopy AAS (Perkin Elmer 5100). At the end of each experiment the produced sludge and the mass loss of the aluminum electrodes were measured.

2.3 Brief description of electrocoagulation

Electrocoagulation is a process consisting of creating metallic hydroxide flocs inside the wastewater by electrodissolution of soluble anodes made of aluminium or iron. The main reactions occurring during electrocoagulation produce aluminium ions at the sacrificial anode and hydroxide ions as well hydrogen gas at the cathode:

\[ \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad \text{(anode)} \]  
\[ 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \quad \text{(cathode)} \]

The generated Al$^{3+}$ and OH$^-$ ions react to form various monomeric and polymeric species such as Al(OH)$^{2+}$, Al(OH)$_2$$^{+}$, Al$_2$(OH)$_2$$^{4+}$, Al(OH)$^{3-}$, Al$_6$(OH)$_{15}$$^{3+}$, Al$_7$(OH)$_{17}$$^{4+}$, Al$_8$(OH)$_{20}$$^{7+}$, Al$_{13}$O$_6$(OH)$_{24}$$^{7+}$, Al$_{13}$(OH)$_{34}$$^{3+}$ which finally result in situ formation of gelatinous Al(OH)$_3$ effecting the coagulation and co-precipitation or H$_2$ flotation of particulates from the solution by adsorption (Koby et al., 2003). The aluminum hydroxide flocs act as absorbents for heavy metal ions. Furthermore, heavy metal ions combine with the electro-generated OH$^-$ ions at the cathode and precipitate in form of their insoluble hydroxides. Both phenomena act synergistically leading to a rapid removal of heavy metal pollutants from water.

3. Results and Discussion

3.1 Effects of operating parameters

The electrocoagulation process is affected by several operating parameters, such as initial pH, pollutants concentrations, current density, COD and contact time. In the present study all these have been explored in order to evaluate a treatment technology for nickel, copper, zinc and chromium removal from synthetic solutions and actual electroplating wastewaters.

3.1.1 Initial pH

According to literature (Vik et al., 1984), pH has a considerable effect on the efficiency of the electrocoagulation process. In addition, pH changes during the process dependent on the anode material and the initial pH value of the treated solution. Vik et al. (1984) reported that...
the observed increase of pH at low initial pH (<7) is ascribed to the hydrogen evolution and the generation of OH\(^-\) ions at the cathodes. In alkaline medium (pH>8) the final pH does not change markedly because the generated OH\(^-\) ions at the cathodes are consumed by the generated Al\(^{3+}\) ions at the anode forming the needed Al(OH)\(_3\) flocs. Furthermore, OH\(^-\) ions can also partially combine with the Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\) and Cr\(^{3+}\) ions to form the insoluble hydroxide precipitates Ni(OH)\(_2\), Cu(OH)\(_2\), Zn(OH)\(_2\) and Cr(OH)\(_3\) respectively. For this reason, in alkaline medium no pH increase but a slight pH decrease was recorded. (Fig. 1).

Experiments were conducted using solutions of Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\) and Cr\(^{6+}\) of 50 mg/L each in the initial pH range 2-9. As can be obtained from Fig. 1 the removal efficiency of all studied metals after 20 minutes of electrolysis time at the constant current density of 20 mA/cm\(^2\) reached very high values, >97% for Cu\(^{2+}\), Ni\(^{2+}\), Zn\(^{2+}\) and >80% for Cr\(^{6+}\) respectively in the pH range 4-10. The removal percent for nickel, copper and zinc is very low at pH<2. It increases considerably at pH 4, remains high and almost constant in the pH range 4-9 and slightly decreases at pH>10. The removal percent of chromium declines substantially at pH>8.

![Figure 1](image)

Figure 1: Removal efficiency of metal ions versus initial pH.

The decrease in removal efficiency at strong acidic and alkaline pH was described by other researchers (Adhoum et al., 2004; Vasuderan et al. 2009). It was ascribed to an amphoteric behavior of Al(OH)\(_3\) which leads to soluble Al\(^{3+}\) cations (at acidic pH) and to monomeric anions Al(OH)\(_4\)^- (at alkaline pH). It is well known that these species are not useful for water treatment. For these reasons the electrocoagulation process was conducted in the pH range 4-8.

3.1.2 Current density

It is well known that the current density determines the coagulant dosage rate, the bubble production rate and size and the floc growth resulting in a faster removal of pollutants (Khosla et al., 1991; Holt et al., 2002). Measurements were carried out at different current densities 10, 20 and 40 mA/cm\(^2\), with the same concentration of 300 mg/L of each metal in aliquot solution of pH = 7. According to Figs 2a,b,c,d the removal rates of all studied metals increased, as expected, with increasing current density. The removal rates of nickel, copper and zinc are very similar showing only a slight preference for zinc followed by copper and nickel.
The removal mechanism of chromium is somehow different. Hexavalent Cr(VI) ions must first be reduced to trivalent Cr(III) ions at the cathode, according to reaction (3), which then combine with the generated OH ions and precipitate as insoluble Cr(OH)₃ or is adsorbed on the Al(OH)₃ flocs.

\[
\text{Cr}_2\text{O}_7^{2-} + 6e^- + 7\text{H}_2\text{O} \rightarrow 2\text{Cr}^{3+} + 14\text{OH}^- \quad (3)
\]

Consequently, the removal rate of chromium is somehow slower (Fig. 2d).

Copper, beyond hydroxide precipitation and absorption on the Al(OH)₃ flocs, is also partially removed by direct electroreduction at the cathode or by electroless deposition according to the reaction (4):

\[
3\text{Cu}^{2+} + 2\text{Al} \rightarrow 3\text{Cu} + 2\text{Al}^{3+} \quad (4)
\]

The electroless deposition occurs mainly at the anode where, due to electrodissolution, the aluminum surface is more active than that of the cathode (Emamjomeh and Sivakumar 2009). A dark brown solid deposit of elemental copper is observed mainly in the vicinity of the anode.
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3.1.3 Initial metal ion concentrations

At current densities of 40, 20 and 10 mA/cm² the initial concentrations of 300 mg/L of nickel, copper and zinc fell under the permissible limits for effluent discharge (2 mg/L) in 50, 80 and 130 minutes respectively. At the same current densities the corresponding concentration of chromium was effectively reduced in 70, 110 and 170 minutes.

Figure 2: Concentration variation with time of a) Ni²⁺, b) Cu²⁺, c) Zn²⁺ and d) Cr⁶⁺ ions at different current densities in aliquot solutions containing 300 mg/L of each metal.

At current densities of 40, 20 and 10 mA/cm² the initial concentrations of 300 mg/L of nickel, copper and zinc fell under the permissible limits for effluent discharge (2 mg/L) in 50, 80 and 130 minutes respectively. At the same current densities the corresponding concentration of chromium was effectively reduced in 70, 110 and 170 minutes.

3.1.3 Initial metal ion concentrations

To demonstrate the effect of initial metallic pollutants concentration and the time required for their quantitative removal, a set of experiments were conducted with three different aliquot solutions containing same concentrations of 300, 150 and 75 mg/L of each metal ion respectively. The mixed solutions were treated at a constant current density of 40 mA/cm² and different times of electrolysis. Figs 3a,b,c,d show the variations of the initial concentrations of nickel, copper, zinc and chromium with time. The three different initial
concentrations of 300, 150 and 75 mg/L of nickel, copper and zinc in the aliquots were reduced to admissible levels after 50, 40 and 20 respectively. The corresponding concentrations of Cr needed 70, 60 and 40 minutes to be quantitatively removed. According to Figs 3a,b,c,d, no direct correlation exists between metal ion concentration and removal efficiency. Certainly, for higher concentrations longer time for removal is needed, but higher initial concentrations were reduced significantly in relatively less time than lower concentrations. The electrocoagulation process is more effective at the beginning when the concentration is higher than at the end of the operation when the concentration is low.
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3.2 Treatment of actual wastewater

The applicability of the electrocoagulation process for actual wastewater was validated by treating an industrial effluent sample, collected from an electroplating unit. The main characteristics of the effluent sample before and after the electrocoagulation treatment are shown in Table 1.

Table 1: Characteristics of the electroplating wastewater before and after the electrocoagulation treatment.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>before treatment</th>
<th>after treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.2</td>
<td>6.3</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>4.0</td>
<td>3.2</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>486</td>
<td>119</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>376</td>
</tr>
<tr>
<td>Cu</td>
<td>283</td>
</tr>
<tr>
<td>Zn</td>
<td>75</td>
</tr>
<tr>
<td>Cr</td>
<td>167</td>
</tr>
</tbody>
</table>

The relatively high COD content of the wastewater indicates the presence of organic compounds added to the electroplating baths as brighteners, levelers, complexing and wetting agents.

At a constant current density of 40 mA/cm² and an electrolysis time of 60 minutes the concentrations of all metals (Ni, Cu, Zn and Cr) fell under the admissible limits, as can be obtained from Fig. 4.

![Figure 4: Concentration variation with time of nickel, copper, zinc and chromium present in the electroplating rinse-water sample.](image)

Compared to the removal from synthetic solutions (Figs 2a,b,c,d) the removal rates of the studied metals from wastewater seem to be slower. This should be attributed to the presence of the organic compounds, which also compete for absorption on the Al(OH)₃ flocs resulting in a substantial reduction of the metal ions removal. The initial COD of 486 mg/L decreased to less than 120 mg/L after 100 minutes showing a removal efficiency of about 75 %. It reached then a plateau and remained almost constant at longer electrolysis time (Fig. 5).

![Figure 5: Removal of COD versus time from the industrial wastewater.](image)
During the electrocoagulation treatment of the wastewater, pH was found to increase at the first few minutes of the operation and changed only slightly afterwards up to 70 minutes of operation time (Fig. 6). The pH increase at the beginning could be attributed to the generation of OH⁻ ions dissociated from water at the cathode according to Eq. 2. The relative stability of pH afterwards could be probably due to the formation of the insoluble Al(OH)₃ flocs and the rest metal hydroxides as pointed out in section 3.1.1.

**Figure 6**: pH variation with time in the industrial wastewater.

Electrocoagulation is a safe, reliable and efficient method for removal of, both, heavy metals and organics from electroplating wastewaters.

### 3.3 Electrode mass loss and energy consumption

To determine the amount of the aluminum mass loss, the electrocoagulation process was repeated with the same operating conditions and changing only the synthetic wastewater for an aqueous solution containing the same NaCl concentration. The generated Al(OH)₃ flocs were dissolved in 4N HNO₃ before the analysis by atomic absorption spectroscopy. Figure 7 shows the experimental and the theoretical faradaic (equation 5) amount \( m_{Al} \) of the dissolved aluminum versus time.

\[
m_{Al} = \frac{I \cdot t \cdot M}{z \cdot F}
\]

where
- \( I \) = current intensity (A)
- \( t \) = time (s)
- \( M \) = Molecular weight of aluminum (g/mol)
- \( z \) = number of electrons transferred in the reaction \( \text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^- \)
- \( F \) = Faraday’s constant (96500 Cb/mol).

The experimentally measured concentration of aluminum is higher than the theoretically expected. This is attributed to chemical dissolution beyond electrodissolution of the aluminum electrodes (Canizares et al., 2009). The generation of \( \text{O}_2 \) and \( \text{H}_2 \) gases during the...
electrolysis makes the solution acidic and alkaline in the vicinity of the anode and the cathode surface respectively. Aluminum, as known, dissolves in both, acidic and alkaline media.

**Figure 7:** Comparison of experimental and theoretical mass loss \( m_{Al} \) of aluminum electrode versus time.

The costs in wastewater treatment with electrocoagulation are the expenditure on mass loss of electrodes and the electrical energy consumption. The mass loss per liter of the aluminum anode \( m_{Al} / L \) (concentration \( c_{Al} \)) during the wastewater treatment can be calculated from equation (6) using the Faraday’s law:

\[
m_{Al} = c_{Al} = \frac{I \cdot t \cdot M}{z \cdot F \cdot V}
\]

where

\( V = \) volume of treated wastewater (L).

Under the operating conditions given the mass loss of the sacrificial aluminum anode for the electrocoagulation is 2.73g Al /L of treated wastewater.

Similarly, the electrical energy consumption \( E \) is calculated from equation (7):

\[
E = \frac{U \cdot I \cdot t}{V}
\]

where

\( U = \) applied voltage (Volts)

The energy consumption amounts to 0.041 Kwh/L of treated wastewater.

**3.4 Sludge characteristics**

The precipitated sludge was collected, dried at 103 °C for 24 h, cooled in a desiccator and weighed. Its amount is determined by the Faraday’s law. The electrocoagulation treatment produces apparently lower amounts of sludge compared to the conventional chemical precipitation - coagulation processes.
4. Conclusions

Electrocoagulation with aluminum electrodes is a safe and convenient route for effective removal of heavy metals, such as copper, nickel, zinc and chromium from synthetic solutions and actual wastewater. Best removal capacity for all studied metals was achieved in the pH range 4-8. Removal rate increased with increasing current density. Nickel, copper and zinc were faster removed than hexavalent chromium. Dissolved organic compounds and COD present in electroplating wastewater were also removed. In comparison to chemical coagulation, where an increased coagulant dosage and several hours are needed, electrocoagulation is a faster and more economical method for removing metallic and organic pollutants from water and industrial effluents.

5. References


