REMOVAL OF HEXAVALENT CHROMIUM FROM ELECTROPLATING WASTEWATER BY ELECTROCOAGULATION WITH IRON ELECTRODES

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ABSTRACT

The performance of electrocoagulation using iron electrodes for the removal of hexavalent chromium from synthetic aqueous solutions and actual industrial electroplating wastewater was studied. Parameters affecting the electrocoagulation process, such as initial pH, applied current density, initial metal ion concentration, COD and time of electroprocessing were investigated. The optimum pH was found to be in the range 4-8. Initial chromium concentrations of $200 - 800$ mg L^{-1} did not influence its removal rate. Higher concentrations were reduced significantly in relatively less time than lower concentrations. 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 40 mA cm^{-2}. The electrocoagulation process was successfully applied to the treatment of an electroplating wastewater sample. Its Cr (VI) ion concentration and COD were effectively reduced under the admissible limits in 50 minutes of electroprocessing.
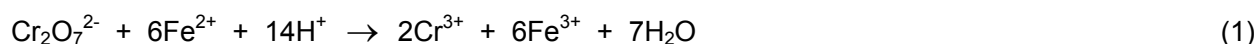
KEYWORDS: electrochemical coagulation, electroplating effluent, hexavalent chromium, iron electrode.

1. INTRODUCTION

Heavy metals, such as mercury, lead, chromium, nickel, copper, cadmium and zinc, are of considerable concern because they are non-biodegradable, highly toxic and probably carcinogen. 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 and Szlag, 2004), electrodialysis (Marder *et al.*, 2004), electrodeionization (Yeon *et al.*, 2003; Lu *et al.*, 2010), membrane-less electrostatic shielding electrodialysis/electrodeionization Dermentzis *et al.*, 2010) and electrocoagulation.

Chromium is released into the environment from electroplating, anodizing, chromating, metal finishing, tannery, dying and fertilizer industries (Liu *et al.*, 2011; Vasudevan *et al.*, 2010). Waste streams from electroplating units may contain up to 2500 mg L^{-1} Cr (VI), which according to environmental regulations worldwide must be controlled to an acceptable level before being discharged to the environment. The permissible limits for Cr (VI) is 0.5 mg L^{-1} in effluent discharge to sewage systems and 0.1 mg L^{-1} in drinking water.

The most common and economical method for hexavalent chromium removal involves reduction to its trivalent state and subsequent precipitation with alkali. As reducing agents are used ferrous ions, sulfur dioxide, sodium bisulfite or hydrazinium salts. The reduced trivalent chromium is then precipitated by addition of an alkali e.g. lime or caustic soda according to reactions (1), (2) and (3):

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \qquad (1)$$
$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3 \qquad (2)$$
$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \qquad (3)$$

The produced sludge amount in the above process is very large, since for 1 kg of chromium removed 32 kg of sludge is generated, which is difficult to handle (Reddithota *et al.,* 2007).

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 polyelectrolytes to remove colloidal matter as gelatinous hydroxides. Also this wastewater treatment process produces a large amount of sludge.

Electrochemical coagulation or otherwise called electrocoagulation uses no chemicals as coagulating agents. These are generated during the electrolysis process by electrodissolution of a sacrificial anode made of aluminum or iron. Electrocoagulation has been successfully performed for treatment and remediation of textile wastewaters (Dermentzis *et al.*, 2011; Kobya *et al.*, 2003; Raju *et al.*, 2008), oil wastes (Abdelwahab *et al.*, 2009; Un *et al.*, 2009), diary effluents (Tchamango *et al.*, 2010), diesel and bio-diesel wastewaters (Chavalparit & Ongwandee, 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 (Adhoum *et al.*, 2004; Heidmann & Calmano 2008; Kongsricharoern & Polprasert, 1996; Nouri *et al.*, 2010).

The objective of this paper was to investigate the efficiency of electrocoagulation in removing hexavalent chromium from synthetic aqueous solutions and actual industrial wastewater. In addition, the effect of pH, current density, initial metal concentration, time of electroprocessing and COD was investigated.

2. METHODS

2.1 Chemicals

KCl, $K_2Cr_2O_7$ 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.) was used to maintain constant DC current. Voltage and current were measured by a multimeter (PHYWE). Conductivity was measured by means of a conductometer (WTW). pH and temperature were measured using a Hanna pH-meter connected to a combined electrode comprising a temperature sensor.

The chemical oxygen demand (COD) was analyzed using a COD reactor (Thermoreaktor TR 420, MERCK) and a direct reading spectrophotometer (Spectroquant Pharo100, MERCK).

Electrochemical experiments were conducted at room temperature in a cylindrical glass cell of 400 ml in which aliquot solutions of 200 mL were placed and slowly stirred with a magnetic bar at 500 rpm. Two commercially obtained iron plates were used as electrodes with size 10cm x 5cm x 0.2cm immersed to a 6 cm depth with an effective area of 30 cm^2 each. The interelectrode distance was 1.5 cm. To remove the oxide and passivation layer from iron surface the electrodes were grinded with sandpaper and energized by dipping them in HCl 5N for 1 minute. 0.5 g KCl was added to every treated solution. The added KCl served for prevention of passivation on the iron 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, filtered using Whatman filter paper (Grade 40). The residual chromium concentrations were determined by Atomic Absorption Spectroscopy AAS (Perkin Elmer 5100). At the end of each experiment the produced sludge was measured.

2.3 Brief description of electrocoagulation

Electrocoagulation is a process consisting of creating metallic hydroxid flocs inside the wastewater by electrodissolution of soluble anodes made of aluminum or iron. The electrochemical oxidation of iron anodes produces ferrous, Fe^{2+} and ferric, Fe^{3+} ions. The Fe^{2+} ions can reduce Cr (VI) to Cr (III) in alkaline to neutral medium, while they are oxidized to Fe^{3+} ions according to reaction (4):

$$CrO_4^{2-} + 3Fe^{2+} + 4H_2O + 4OH^- \rightarrow 3Fe(OH)_3 + Cr(OH)_3 \qquad (4)$$
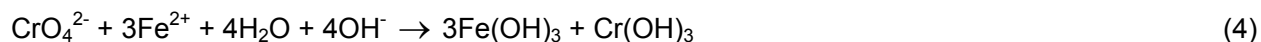
Both, Fe^{3+} and Cr^{3+} ions combine with the generated OH- ions and precipitate as insoluble hydroxides. The Fe^{2+} ions can also reduce $Cr_2O_7^{2-}$ ions in acidic medium according to reaction (1), as already stated. The generated H_2 gas produced at the cathode can remove dissolved organics or any suspended material by flotation. Furthermore, Fe^{3+} ions undergo hydration and give, depending on pH, cationic species such as $Fe(OH)^{2+}$, $Fe(OH)_2^{2+}$ in acidic conditions, $Fe(OH)_3$ in neutral conditions and anionic species such as $Fe(OH)_4^-$, $Fe(OH)_6^{3-}$ in alkaline conditions which finally result in situ formation of gelatinous $Fe(OH)_3$ effecting the coagulation and co-precipitation from the solution by adsorption. The iron hydroxide flocs act as adsorbents 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. Fe^{3+} as a flocculation agent is advantageous, due to its innocuity compared to Al^{3+}, which shows some toxic effects.

3. RESULTS AND DISCUSSION

3.1 Effects of operating parameters

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

3.1.1 Initial pH

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. The increase of pH at initial pH lower than 7 is ascribed to the hydrogen evolution and the generation of OH⁻ ions at the cathodes (Vik *et al.,* 1984). 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 Fe^{3+} ions at the anode forming the needed $Fe(OH)_3$ flocs. Furthermore, OH⁻ ions can also partially combine with Cr^{3+} ions to form the insoluble hydroxide precipitate Cr $(OH)_3$.

Experiments conducted at different initial pH values in the range 1-10 showed that the removal percent of chromium is low at pH<2. It increases considerably at pH 4, remains high and almost constant in the pH range 4-8 and substantially decreases at pH>8. The decrease in removal efficiency at strong acidic and strong alkaline pH was described by other researchers (Adhoum *et al.*, 2004; Vasudevan *et al.* 2009). It was ascribed to an amphoteric behavior of $Fe(OH)_3$ which leads to soluble cations Fe^{3+} , $Fe(OH)^{2+}$, $Fe(OH)_2^+$ (at acidic pH) and to monomeric anions $Fe(OH)_4^-$, $Fe(OH)_6^{3-}$ (at alkaline pH). It is well known that these species are not usefull for water treatment. For these reasons the electrocoagulation process was conducted in the pH range 4-8.

3.1.2 Current density

Khosla *et al.* (1991) reported that the applied current density determines the coagulant dosage rate, the bubble production rate and size and the flocs growth resulting in a faster removal of pollutants. Measurements were carried out at different current densities 10-40 mA cm⁻², at a constant heavy metal concentration of 800 mg L⁻¹ and initial pH 7.5. According to Fig. 1 the removal rate of chromium increased, as expected, with increasing current density. After 40 minutes of electrolysis time at the current density 40 mA cm⁻², Cr (VI) ions have been almost quantitatively removed (>99%) and their concentration decreased under the admissible limits for effluents discharge to sewage systems (0.5 mg L⁻¹).
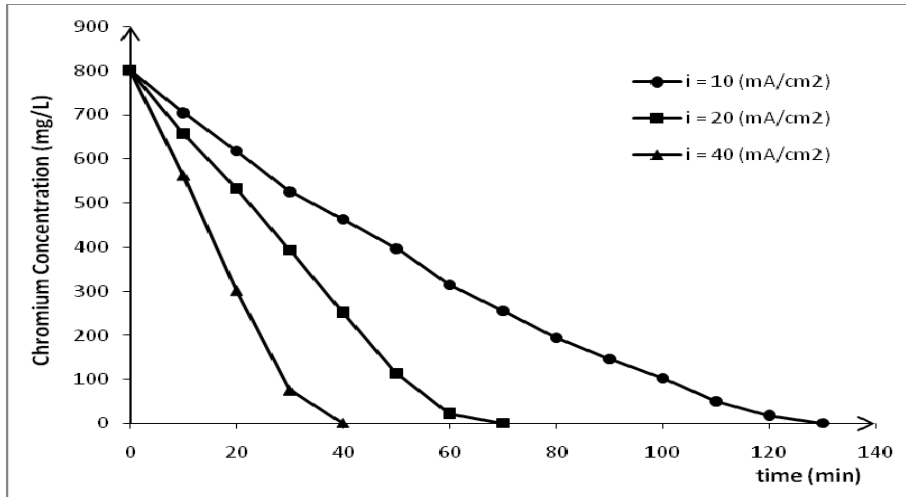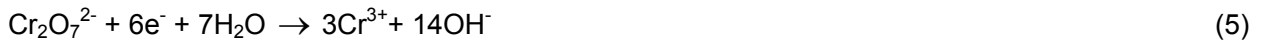
Figure 1. Chromium concentration versus time at different current densities

Cr (VI) ions must first be reduced to Cr (III) ions at the cathode, according to reaction (5), which then combine with the generated OH$^-$ ions and precipitate as insoluble Cr (OH)$_3$ or are adsorbed to the Fe(OH)$_3$ flocs.

$$Cr_2O_7^{2-} + 6e^- + 7H_2O \rightarrow 3Cr^{3+} + 14OH^- \tag{5}$$

Furthermore, Cr (VI) ions can also be reduced to Cr (III) ions by Fe (II) ions which in turn are oxidized to Fe (III) ions according the reaction (1) in acidic pH or according to reaction (4) in alkaline to neutral pH, as already stated in the introductory section 1 and 2.3 respectively. The presence of ferrous ions enhances the reduction and removal of chromium. Consequently, the removal rate of chromium by electrocoagulation with iron electrodes is faster compared to that with aluminium electrodes.

3.1.3 Initial metal ion concentration

To demonstrate the effect of initial metallic pollutant concentration and the time required for its quantitative removal, a set of experiments was conducted with different initial concentrations 200, 400 and 800 mg L^{-1} of chromium ions. Each solution was treated at a constant current density of 40 mA cm^{-2} and different times of electrolysis.
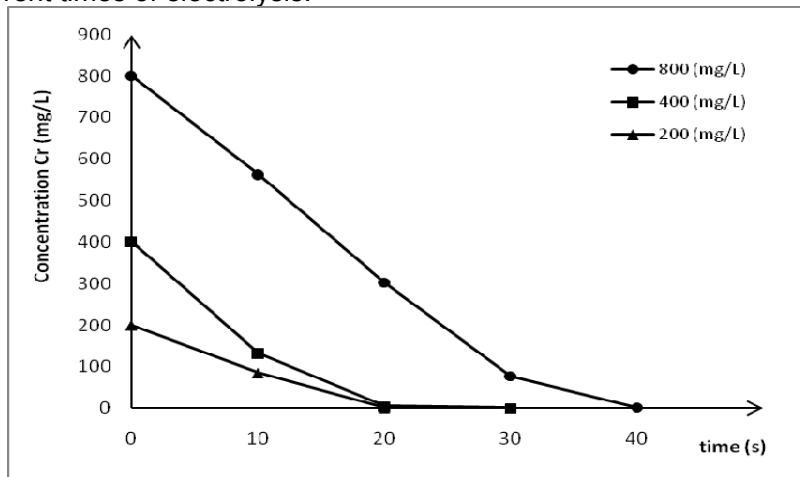

Figure 2. Effect of initial concentration of chromium on its removal efficiency versus time

Fig. 2 shows the variations of the different initial concentrations of chromium and its removal efficiency with time. The three chromium ion concentrations were reduced to admissible levels in 20, 25 and 40 minutes respectively. According to Fig. 2, 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.

3.2 Treatment of actual wastewaters

The applicability of the electrocoagulation process for actual wastewater was validated by treating an industrial effluent sample, collected from an electroplating unit. As known, chromium electrodeposits are mainly obtained from acidic hexavalent chromium electrolytic baths. During the plating process Cr (VI) ions contaminate the rinse waters when the plated objects are rinsed upon removal from the plating bath.

At a constant current density of 40 mA cm^{-2} and an electrolysis time of 50 minutes the concentration of chromium decreased under the admissible limits (Fig. 3). The removal efficiency *re* is very high (99.9 %). It is calculated from the formula of equation 1:

$$re = \frac{C_o - C}{C_o} \times 100 \tag{1}$$

where C_o and C are the initial and final concentrations of chromium ions in the treated wastewater.
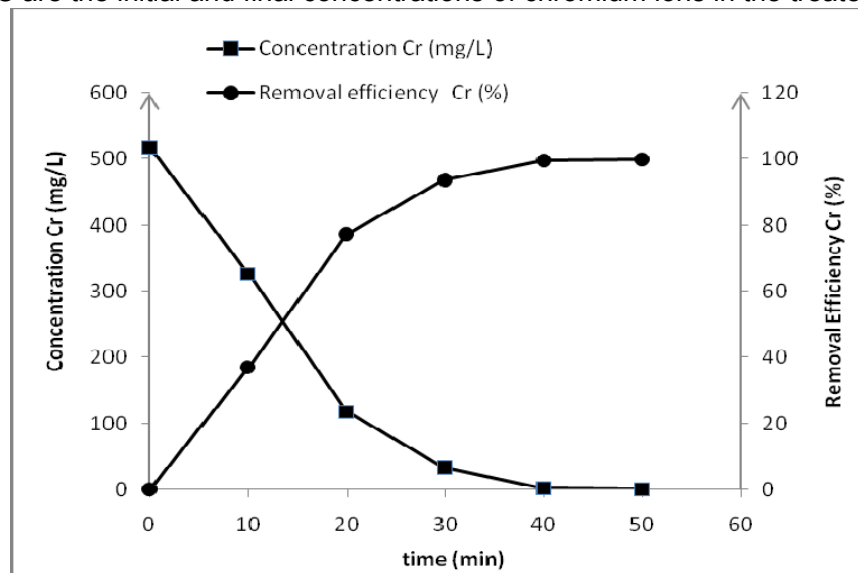

Figure 3. Concentration variation and removal efficiency of chromium versus time during the electrocoagulation treatment of the electroplating wastewater

Compared to the removal from synthetic solutions (Figs 1, 2) the removal rate of chromium from actual wastewater seems to be slower. This should be attributed to the presence of the organic compounds, which also compete for adsorption on the Fe (OH)$_3$ flocs resulting in a substantial reduction of the metal ions removal. The initial COD content of 530 mg L^{-1} decreased to 183 mg L^{-1} after 50 minutes of electroprocessing showing a removal efficiency of about 65.5 %. During the electrocoagulation treatment of the wastewater its initial pH value of 3.5 rose to a final value of 8.4.

3.3 Electrode mass loss and energy consumption

The costs in wastewater treatment with electrocoagulation are the expenditure on mass loss of electrodes and the electrical energy consumption. The mass loss of the iron anode m_{Fe} can be calculated from equation (2) using the Faraday's law:

$$mFe = \frac{I \cdot t \cdot M}{z \cdot F \cdot V} \tag{2}$$

where

I = current intensity (A)
t = time (s)
M = Molecular weight of iron (g mol^{-1})

z = number of electrons transferred in the reaction $Fe \rightarrow Fe^{2+} + 2e^-$
F = Faraday's constant (96500 Cb mol^{-1})
V = wastewater solution volume.

Under the given operating conditions the mass loss of the sacrificial iron anode per liter of the treated wastewater is 4.34 g Fe L^{-1}.

Similarly, the electrical energy consumption E is calculated from equation (3):

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

(3)

Where: U = voltage (Volts).

The energy consumption amounts to 0.046 kWh L^{-1} of treated wastewater.

3.4 Sludge characteristics

The precipitated sludge was collected, dried at 103 $^{\circ}$C for 24 h, cooled in a desiccator and weighed. Its amount was determined by the Faraday's law. Compared to the conventional chemical precipitation - coagulation process, electrocoagulation produces apparently lower amount of sludge.

4. CONCLUSIONS

Electrocoagulation with iron electrodes is a safe, reliable, convenient and efficient route for removal of heavy metals, such as chromium and COD from water and industrial wastewater. Best removal efficiency was achieved in the pH range 4-8. Removal rate increased with increasing current density. Initial chromium concentration of 200, 400, 800 mg L^{-1} in synthetic solutions and 517 mg L^{-1} in industrial wastewater at a current density of 40 mA cm^{-2} reduced under the admissible limits in a short period of time. Furthermore, the COD in electroplating wastewater was 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 wastewater treatment.

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