REMEDIATION OF HEAVY METAL BEARING WASTEWATER BY PHOTOVOLTAIC ELECTROCOAGULATION

Konstantinos Dermentzis, Dimitrios Marmanis, Achilleas Christoforidis

Department of Petroleum & Natural Gas Technology, Kavala Institute of Technology, 65404 Agios Loucas, Kavala, Greece Tel +30 2510 245133, Fax: +30 2510 245133 E-mail: demerz@otenet.gr

Abstract

In this study a photovoltaic electrocoagulation (PV-EC) process is proposed, which combines the autonomous and environmentally friendly photovoltaic solar energy with the capability of iron electrocoagulation to effectively remove heavy metals, such as chromium, nickel and copper from industrial electroplating effluents. The photovoltaic array can be connected directly to the electrocoagulation reactor without batteries increasing, in this way, the system sustainability and eliminating the environmental threat of improper battery disposal. The PV-EC system is made versatile according to the instantaneous solar irradiation by adjusting the wastewater flow rate to the current intensity supplied by the photovoltaic array. All operating parameters affecting the efficiency of the proposed process, such as wastewater conductivity, pH, flow rate, current density, electroprocessing time and solar irradiance were studied and optimal conditions were investigated. The experimental results showed that by applying a current density of 30 mA/cm^2 the concentrations of chromium, nickel and copper in the treated electroplating wastewater were effectively reduced from their corresponding initial values of 86, 65 and 37 mg/L to less than the permissible limit, amounting to a removal percentage of over 99%. The corresponding electrical energy consumption was 15 kWh per m^3 of treated wastewater. The proposed process is appropriate for remediating industrial effluents laden with heavy metals and especially for applications in remote and isolated locations without connection to the public electrical system.

Keywords: electrochemical coagulation; electroplating effluents; chromium; nickel; copper; photovoltaic solar energy
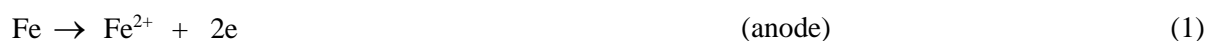
1. INTRODUCTION

Industrial effluents originating mainly from electroplating industries contain high amounts of heavy metal ions (Cr, Ni, Cu, Cd, Zn). These heavy metal bearing wastewaters are of considerable concern because they are non-biodegradable, highly toxic and probably carcinogen. 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.

Several treatment processes have been suggested for the removal of heavy metals from aqueous waste streams, such as adsorption (Kyzas *et al.,* 2009), biosorption (Farhan *et al.,* 2012), ion exchange (Inglezakis et al., 2003), cathodic reduction (Formari and Abbruzzese, 1999), electrodialysis/ electrodeionization using membranes (Arar *et al.,* 2014; Caprarescu *et al.,* 2011; Ren *et al.,* 2013) or electrostatic shielding (Dermentzis, 2010), chemical coagulation - precipitation and electrocoagulation (Dermentzis *et al.,* 2011; Verma *et al.,* 2013).

The conventional chemical coagulation relies on the decrease of the net surface charge and the electrical double-layer of colloids by the addition of coagulants, such as $FeCl_3$, $Al_2(SO_4)_3$, or organic polyelectrolytes which leads to their coagulation and precipitation.

Electrocoagulation is a new alternative way of coagulation, where the coagulants $Al(OH)_3$ and $Fe(OH)_3$ are not added to the treated solution but are produced in situ by electrodissolution of sacrificial anodes made of aluminum or iron respectively.

During the electrocoagulation process with iron electrodes the chemical reactions (1), (2) and (3) occur. The electrochemically produced Fe^{2+} and Fe^{3+} ions combine with OH^- ions forming the needed coagulants $Fe(OH)_2$ and $Fe(OH)_3$ according to reactions (4) και (5).

$$Fe \rightarrow Fe^{2+} + 2e \qquad \text{(anode)} \qquad (1)$$

$$Fe \rightarrow Fe^{3+} + 3e \qquad \text{(cathode)} \qquad (2)$$

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \qquad \text{(cathode)} \qquad (3)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \tag{4}$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \tag{5}$$

The Fe^{2+} ions can reduce Cr(VI) to Cr(III), while they are oxidized to Fe^{3+} ions according to reaction (6):

$$CrO_4^{2-} + 3Fe^{2+} + 4H_2O + 4OH^- \rightarrow 3Fe(OH)_3 + Cr(OH)_3 \tag{6}$$
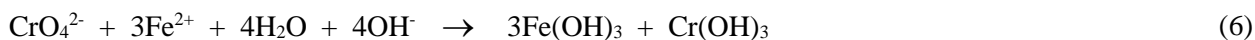
Cr(VI) ions are also reduced to Cr(III) ions at the cathode according to reaction (7):

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

Bivalent heavy metal ions Me^{2+} (Cu^{2+} and $Ni^{2+)}$) and trivalent chromium ions (Cr^{3+}) are removed by adsorption by the coagulants $Fe(OH)_2$ and $Fe(OH)_3$. Furthermore, they combine with the electrochemically (reaction 3) or chemically (reaction 7) generated OH^- ions and precipitate as insoluble hydroxides according to reactions (8) and (9) or:

$$Me^{2+} + 2OH^- \rightarrow Me(OH)_2 \tag{8}$$

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3 \tag{9}$$
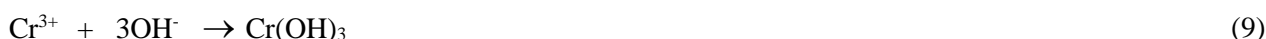
Both phenomena act synergistically leading to a rapid removal of heavy metal pollutants from water.

The electrochemical coagulation process has the advantage of combined phenomena of oxidation, reduction, flotation, adsorption and coagulation. It is effectively applied to treatment of dye house effluents, oil wastes, paper mill and heavy metal bearing effluents.

Increased environmental pollution and social concern about the environment in the last decades have led to the development of new renewable energy forms. The photovoltaic (PV) solar energy is one of the most popular and well studied renewable energy sources, which, as autonomous and environmentally friendly, is appropriate for small applications and especially in remote and isolated locations with lack of electric grid (Irfan, 1997). Electrochemical processes directly powered by photovoltaic energy have been recently reported in literature (Alvarez-Guerra *et al.,* 2011; Ortiz *et al.,* 2007; Valero *et al.,* 2008; Zhang *et al.,* 2013). As we are aware, none of them deals with heavy metal removal from industrial effluents.

The present paper demonstrates the possibility of remediating heavy metal bearing electroplating effluents using electrocoagulation (EC) with iron electrodes, which is directly powered by a PV array without batteries. The photovoltaic electrocoagulation (PV-EC) system is made versatile according to the instantaneous solar irradiation by adjusting the wastewater flow rate to the current density supplied by the PV array. All operating parameters affecting the PV-EC process, such as wastewater pH, current density, conductivity, flow rate, contact time and solar irradiation are determined.

2. METHODS

The actual wastewater was obtained from an electroplating unit located near Thessaloniki, northern Greece, with the main characteristics listed in Table 1.

Table 1. Main characteristics of electroplating wastewater

Parameter:	Value:
pH	4.5
Conductivity	4500 µS/cm (after addition of KCl)
Cr (VI) mg/L	86
Ni (II) mg/L	65
Cu (II) mg/L	37

The photovoltaic module used was SUNPOWER (Maxeon Cell Technology) SPR-327NE-WHT-D made from monocrystalline silicon with a surface area of 1.63 m^2 and a peak power of 327 W. The

experiments were conducted in Kavala Institute of Technology (latitude 40° 55´, longitude 24° 22´ and altitude 138 m above the sea level).

DC voltage and current were measured by a multimeter (PHYWE). Conductivity was measured by means of a conductometer (WTW). The pH and the temperature were measured using a Hanna pH-meter. The wastewater was circulated by a peristaltic pump.

Electrolyses were conducted at room temperature in a cylindrical glass cell of 400 ml in which 200 ml of wastewater were placed and slowly stirred with a magnetic bar at 500 rpm. Three commercially obtained iron plates of size 10cm x 5cm x 0.2cm 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 0.5 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. KCl was added to every treated solution for prevention of passivation on the iron electrode surface and decrease of the excessive ohmic drop in the solution. Samples were extracted every 5 minutes, filtered using Whatman filter paper (Grade 40). The residual heavy metal ion concentrations were determined by Atomic Absorption Spectroscopy AAS (Perkin Elmer 5100).

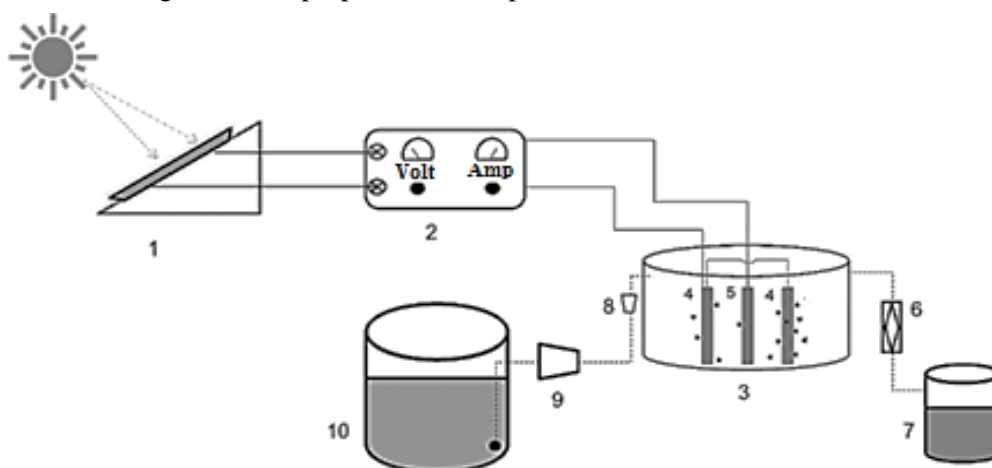Figure 1 shows a flow diagram of the proposed PV-EC process.

Figure 1. Diagram of the experimental setup. 1. PV Solar module 2. Regulator 3. Electrocoagulation reactor 4. Electrode (a) 5. Electrode (b) 6. Filter 7. Treated solution 8. Flow meter 9. Peristaltic pump 10. Wastewater deposit

3. RESULTS AND DISCUSSION
3.1. Effect of operating parameters

The PV-EC process is affected by several operating parameters, such as initial pH, current density, conductivity, flow rate and contact time. In the present study all these parameters have been explored in order to evaluate a treatment technology for chromium, nickel and copper removal from actual electroplating wastewaters.

3.1.1. Effect of initial pH

The initial pH value of the treated solution has a considerable effect on the efficiency of the electrocoagulation process. Experiments were conducted in the pH range 2-10 using separate solutions of 50 mg/L of copper, nickel and chromium respectively. As can be seen in Figure 2, after the electrolysis time of 20 minutes at constant current density of 10 mA/cm^2 the percent removal of all studied metals increases considerably with increasing pH in the range 2-10. In acidic environment (pH<2) the removal is low, whereas it increases considerably at pH 4 and is maintained high in the pH range 4-10. The decrease of removal efficiency in strong acidic medium is due to the formation of the soluble Fe^{2+} and Fe^{3+} ions which, as known (Adhoum *et al*., 2004; Vasudevan *et al.,* 2009), do not favor the coagulation phenomenon.
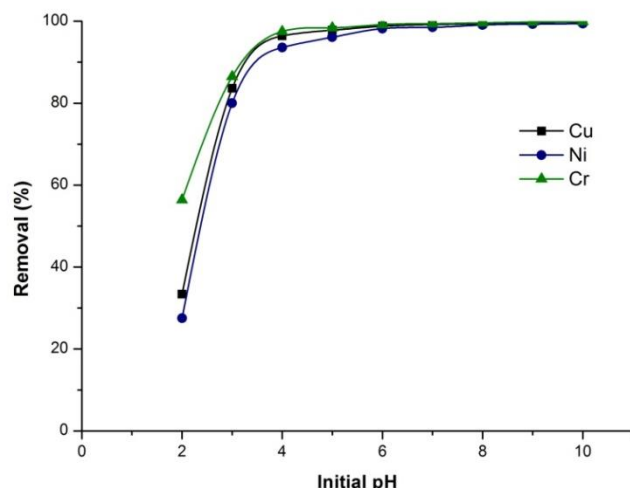
Figure 2. Removal of Cr, Ni and Cu by electrocoagulation versus initial solution pH

3.1.2. Effect of current density

It is well known that the 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 10-30 mA/cm^2, at constant initial heavy metal concentrations of 96, 65, 37 mg/L for Cr, Ni, Cu respectively and initial pH 4.5. According to Table 2, the removal rate of all studied metals increased, as expected, with increasing current density. In 70, 40 and 30 minutes of electrolysis time at the corresponding current densities of 10, 20 and 30 mA/cm^2, chromium, nickel and copper ions have been almost quantitatively removed (>99%) and their concentration fell under the admissible limits for effluents discharge to sewage systems (2 mg/L).

Table 2. Concentration variation of chromium, nickel and copper ions with time at different current densities

| | 10 mA/cm^2 | | | 20 mA/cm^2 | | | 30 mA/cm^2 | | |
| | Concentration (mg/L) | | | Concentration (mg/L) | | | Concentration (mg/L) | | |
Time (min)	Cr	Ni	Cu	Cr	Ni	Cu	Cr	Ni	Cu
0	86.0	65.0	37.0	86.0	65.0	37.0	86.0	65.0	37.0
10	44.5	32.6	19.3	23.5	16.1	8.4	14.5	8.1	5.5
20	17.3	14.4	7.7	7.6	4.0	3.3	1.4	0.3	0.2
30	8.8	6.8	2.3	1.2	0.3	0.2	0.1		
40	4.2	2.5	0.4	0.3					
50	2.6	0.7							
60	0.8	0.3							
70	0.2								

3.1.3. Effect of conductivity

The wastewater conductivity affects immediately the applied voltage and therefore the electrical energy consumption. The removal percentage of all studied heavy metals is hardly affected and remains constant over 99 % for the three tested wastewater conductivities of 1500, 3000 and 4500 μS/cm (Table 3).

Table 3. Electrocoagulation results for different wastewater conductivities

| Conductivity (μS/cm) | Voltage (V) | Energy consumption (kWh/m^3 | Removal percentage (%) | | |
			Cr	Ni	Cu
1500	18.4	64.6	99.3	99.0	99.4
3000	9.5	32.2	99.6	99.3	99.5
4500	5.2	15.0	99.4	99.2	99.1

3.1.4. Effect of flow rate

The current density supplied by the PV array depends on the solar irradiation and the temperature of the PV modules. These parameters cannot be controlled and will change continuously through the hours in a day or suddenly through clouds crossing or changes in wind speed. Ortiz *et al.* 2007 and Valero *et al.* 2008 proposed a clever mode of operation in order to make the PV-EC system versatile to instantaneous solar irradiation by keeping constant the ratio current density/flow rate. Thus, when the current density supplied by the PV array changes, also the working flow rate must proportionally change to maintain this ratio constant. This operation way implies that the volume of treated wastewater is directly related to the solar energy incident on the panels. The experiments with constant current density and flow rate were conducted at a sunny midday and in short periods to keep approximately constant values of solar irradiation. As can be obtained from Table 4, by increasing the current density the cell voltage and flow rate increase proportionally, while the residence time decreases. The removal percentage of all three studied metals is hardly affected and remains high >99 % in all experiments.

Table 4. Electrocoagulation results for different wastewater flow rates

Flow rate (L/h)	Current density (mA/cm^2)	Voltage (V)	Residence time (min)	Removal percentage (%)		
				Cr	Ni	Cu
0.3	10	8.4	40	99.7	99.2	99.5
0.6	20	16.2	20	99.4	99.1	99.3
0.9	30	24.6	13.3	99.3	99.0	99.1

3.2. Solar irradiation and *I-V* curve of photovoltaic module

The solar irradiation intensity depends on the occasional meteorological/geographical conditions and influences the photovoltaic output current and therefore, the performance of the electrocoagulation process. As stated in section 3.1.4, the flow rate of the treated wastewater can be used as the control parameter. The most important characteristics of the current-voltage curve of the photovoltaic module for a solar irradiation of 1000 w/m^2 and temperature of 25°C are given in Figure 3. The short circuit current I_{sc} is the maximum current supplied by the PV panel at zero voltage between terminals. It depends mainly on solar irradiation and amounts to 6.46 Ampere. The open circuit voltage is the maximum voltage reached in absence of load. It depends mainly on temperature and amounts to 64.9 Volt.

4. CONCLUSIONS

This paper shows the feasibility of performing remediation of heavy metals (Cr, Ni, Cu) bearing electroplating effluents by directly connecting the electrocoagulation reactor to the photovoltaic generator. The current density supplied by the PV array depends on the solar irradiation and the temperature of the photovoltaic modules. However, the PV-EC system is made versatile to instantaneous solar irradiation by adjusting the flow rate of the treated wastewater and keeping constant the ratio current density/flow rate. The removal percentage of chromium, nickel and copper remains high (>99 %) for the three tested wastewater flow rates of 0.3, 0.6 and 0.9 L/h and the three wastewater conductivities of 1500, 3000 and 4500 μS/cm. Based on the experimental results, the proposed PV-EC process could present some advantages for wastewater purification applications in isolated places with lack of electric grid. Furthermore, the process avoids problems concerning the maintenance of batteries and increases the system sustainability.
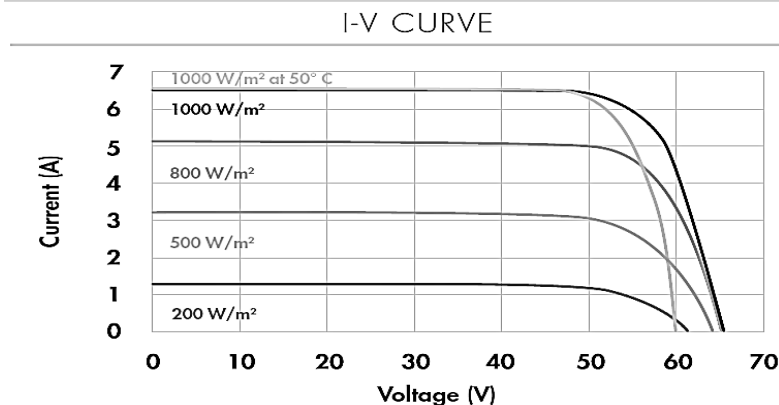

Figure 3. *I-V* curve of photovoltaic module

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