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Photovoltaic electrocoagulation process for remediation of chromium plating wastewaters

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ABSTRACT

The proposed photovoltaic electrocoagulation (PV-EC) process combines the autonomous and environmentally friendly photovoltaic (PV) solar energy with the capability of iron electrocoagulation (EC) to effectively reduce both trivalent and hexavalent chromium ions from electroplating effluents. The PV array can be connected directly to the EC 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 PV array. The experiments were conducted in Kavala Institute of Technology (latitude 40˚ 55´, longitude 24˚ 22´, and altitude 138 m above the sea level). 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 20 mA cm^2, the chromium concentration in the treated electroplating wastewater was effectively reduced from its initial value of 96 mg L^{-1} to less than the permissible limit amounting to a removal percentage of over 99%. The corresponding electrical energy consumption was 8.4 kWh per m^3 of treated wastewater. The proposed process is appropriate for removal of chromium from industrial effluents and especially for small applications in remote and isolated locations with lack of electric grid.

Keywords: Electrochemical coagulation; Electroplating effluents; Hexavalent chromium; Heavy metals; Photovoltaic solar energy

1. Introduction

Chromium is released into the environment from electroplating, anodizing, chromating, metal finishing, tannery, dyeing, and fertilizer industries. Waste streams from electroplating units usually contain about 100 mg/L 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 2 mg L^{-1} in effluent discharge to sewage systems and 0.1 mg L^{-1} in drinking water.

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Several treatment processes have been suggested for the removal of trivalent and hexavalent chromium from aqueous waste streams: adsorption [1], biosorption [2], ultrafiltration [3], ion exchange [4] and electrochemical methods: cathodic reduction [5–7], electrodialysis–electrodeionization [8–10], membraneless electrostatic shielding electrodialysis [11], and electrocoagulation (EC) [12–16].

Chemical coagulation is a quite effective method for treating chromium and other 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. In addition, the process produces large amounts of sludge.

EC is a process consisting of creating metallic hydroxide 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), while they are oxidized to Fe^{3+} ions according to reaction (1):

$$CrO_4^{2-} + 3Fe^{2+} + 4H_2O + 4OH^- - \\ \rightarrow 3Fe(OH)_3 + Cr(OH)_3 \tag{1}$$

Both, Fe^{3+} and Cr^{3+} ions combine with the generated OH^- ions and precipitate as insoluble hydroxides. 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, neutral $Fe(OH)_3$ in neutral conditions, and anionic species such, as $Fe(OH)_{4-}$, $Fe(OH)_6^{3-}$, in alkaline conditions, which finally results *in situ* formation of gelatinous $Fe(OH)_3$ effecting the coagulation and coprecipitation from the solution by adsorption. The iron hydroxide flocs act as absorbents for chromium and other heavy metal ions. Both phenomena act synergistically leading to a rapid removal of heavy metal pollutants from water.

Cr(VI) ions are also reduced to Cr(III) ions at the cathode according to reaction (2), which then combine with the cathodically or chemically generated OH^- ions and precipitate as insoluble $Cr(OH)_3$ according to reaction (3) or are adsorbed to the $Fe(OH)_3$ flocs.

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

$$Cr^{3+} + 3OH^- \longrightarrow Cr(OH)_3 \tag{3}$$

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 [17]. Electrochemical processes, directly powered by PV energy, have been recently reported in literature [18–21]. As we are aware, none of them deals with chromium removal from industrial effluents.

The present paper demonstrates the possibility of remediating chromium bearing plating effluents using 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. Materials and methods

The actual wastewater was obtained from an electroplating unit located near Thessaloniki, northern Greece, with the main characteristics pH 4.5, Cr(VI) concentration 96 mg/L, and conductivity 4,000 μS/cm (after addition of KCl electrolyte).

The PV 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 was placed and slowly stirred with a magnetic bar at 500 rpm. Three commercially obtained iron plates of size 10 × 5 × 0.2 cm, immersed to a 6-cm depth with an effective area of 30 cm^2 each, were used as electrodes in the experiments. The interelectrode 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 5 N for 1 min. 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 2.5 min, filtered using Whatman filter paper (Grade 40). The residual

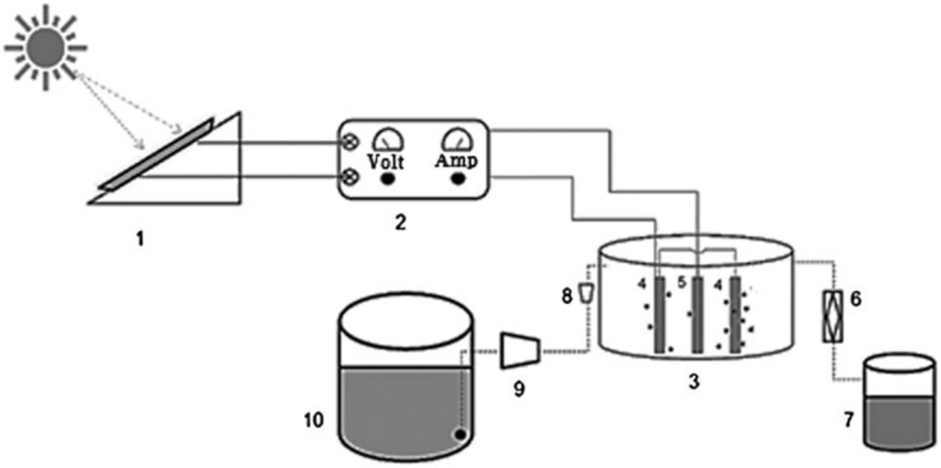

Fig. 1. Diagram of the experimental setup. (1) PV solar module, (2) regulator, (3) **EC** reactor, (4) electrode (a), (5) electrode (b), (6) filter, (7) treated solution, (8) flow meter, (9) peristaltic pump, and (10) wastewater deposit.

total trivalent and hexavalent chromium concentrations were determined by Atomic Absorption Spectroscopy AAS (Perkin Elmer 5100).

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

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 removal from actual electroplating wastewaters.

3.1.1. Effect of initial pH

In our previous work [16], the treatment of Cr(VI)-containing electroplating wastewater was optimized by means of conventional EC. It was found 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 decreases at pH > 8. The decrease in removal efficiency at strong acidic and strong alkaline pH was described by Adhoum et al. [22]. The value of pH changes during the process dependent on the anode material and the initial pH of the treated solution. 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 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 $Cr(OH)_3$. For these reasons, the EC process was conducted in the pH range 4–8.

3.1.2. Effect of current density

Khosla et al. [23] reported 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 a constant heavy metal concentration of 96 mg/L and pH 4.5. According to Fig. 2, the removal rate of chromium increased, as expected, with increasing

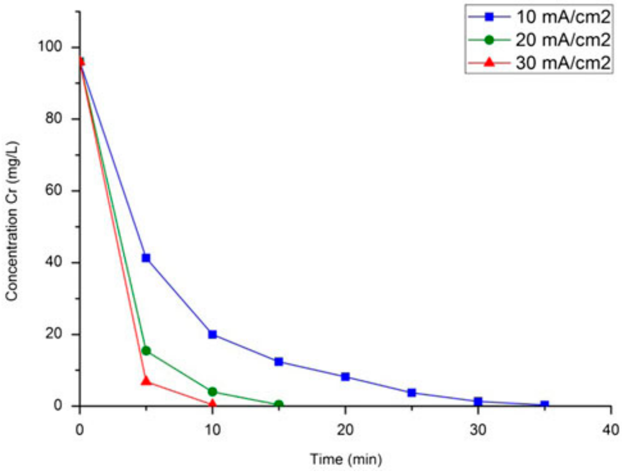

Fig. 2. Concentration variation of chromium ions with time at different current densities.

Table 1
EC results for different wastewater conductivities

Conductivity (μS/cm)	Voltage (V)	Energy consumption (kWh/m^3)	Removal percentage (%)
1,000	24.5	36.7	99.2
2,000	12.2	18.3	99.6
4,000	5.8	8.4	99.3

current density. In 35, 15, and 10 min of electrolysis time at the corresponding current densities of 10, 20, and 30 mA/cm^2, chromium ions have been almost quantitatively removed (>99%) and their total concentration fell under the admissible limits for effluents discharge to sewage systems.

3.1.3. Effect of conductivity

The wastewater conductivity affects immediately the applied voltage, and therefore the electrical energy consumption. The removal percentage of chromium is hardly affected and remains constant over 99% for the three tested wastewater conductivities of 1,000, 2000, and 4,000 μS/cm (Table 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. and Valero et al. [19,20] 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, the working flow rate must also 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 2, by increasing the current density, the cell voltage and flow rate increase proportionally, while the residence time decreases. The removal percentage of chromium is hardly affected and remains high >99% in all experiments.

3.2. Energy consumption, electrode mass loss, and sludge production

The costs in wastewater treatment with EC 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 Eq. (2) using the Faraday's law:

$$m_{\mathrm{Fe}} = \frac{I \cdot t \cdot M}{z \cdot F \cdot V} \tag{4}$$

where I = current intensity (A); t = time (s); M = molecular weight of iron (g/mol); z = number of electrons transferred; F = Faraday's constant (96,500 Cb/mol); and V = wastewater solution volume.

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

$$E = \frac{U \cdot I \cdot t}{V} \tag{5}$$

where U = voltage (V).

The mass loss of the sacrificial iron anode and the energy consumption after the EC treatment of the wastewater sample of 4,000 μS/cm at a current density of 20 mA/cm^2 and chromium elimination of 99%

Table 2
EC results for different wastewater flow rates

Flow rate (L/h)	Current density (mA/cm^2)	Voltage (V)	Residence time (min)	Removal percentage (%)
0.5	10	6.7	24	99.7
1.0	20	12.2	12	99.6
1.5	30	18.4	8	99.3

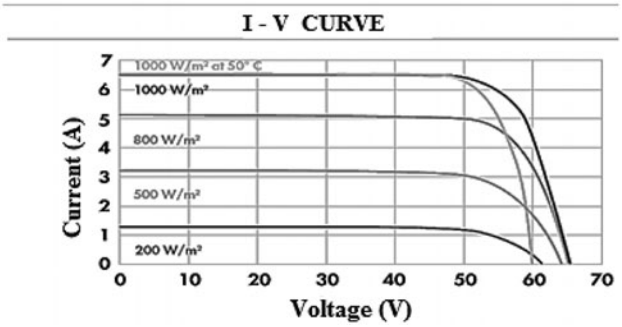

Fig. 3. *I–V* curve of PV module.

amount to 1.044 kg and 8.4 kWh per m^3 of treated wastewater, respectively (Table 1).

The precipitated sludge was collected, dried at 103˚C for 24 h, cooled in a desiccator and, weighed. Its amount was 2.43 kg dried sludge per m^3 of treated wastewater.

3.3. *Solar irradiation and* I–V *curve of PV module*

The solar irradiation intensity depends on the occasional meteorological/geographical conditions and influences the PV output current, and therefore the performance of the EC 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 PV module for a solar irradiation of 1,000 w/m^2 and temperature of 25˚C are given in Fig. 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 A. The open-circuit voltage is the maximum voltage reached in absence of load. It depends mainly on temperature and amounts to 64.9 V.

4. Conclusion

This paper shows the feasibility of performing remediation of chromium electroplating effluents by directly connecting the EC reactor to the PV generator. The current density supplied by the PV array depends on the solar irradiation and the temperature of the PV 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 remains high (>99%) for the three tested wastewater flow rates of 0.5, 1.0, and 1.5 L/h and the three wastewater conductivities of 1,000, 2,000, and 4,000 μS/cm. Based on the experimental results, the proposed PV-EC process could present some advantages for wastewater purification applications in isolated places with a lack of electric grid. Furthermore, the process avoids problems concerning the maintenance of batteries and increases the system sustainability.

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