Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2021.26722

213 (2021) 371–380
February

Nickel and chromium removal by electrocoagulation using copper electrodes

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Received 25 March 2020; Accepted 17 October 2020

ABSTRACT

Synthetic and real wastewater, containing nickel (Ni) and hexavalent chromium (Cr(VI)), have been treated using electrocoagulation, under various operating conditions. The treatment process of electrocoagulation was performed using copper electrodes. The following parameters were examined to study their effects upon the treatment process: initial pH values, current densities, electrolysis times, the spacing between electrodes, modes of operation (batch vs. continuous), and electrolyte types. The results showed that the best removal efficiencies for Ni and Cr(VI) were obtained at pH = 9.2; current density = 5–10 mA/cm^2; and an electrode spacing of 4 cm, using NaCl as the electrolyte. Ni and Cr removal efficiencies reached 99.96% and 98%, respectively. Batch and continuous modes of operation achieved almost the same removal efficiency, while the batch mode consumed more electrical energy. Compared with electrocoagulation, chemical coagulation using copper salts demonstrated lower removal efficiencies for both Ni and Cr. Scanning electron microscopy was used to assess the morphology of the electrodes. The electrical energy cost varied from 0.8–3 US\$/m^3, while the material cost totaled around 0.003 US\$/m^3.

Keywords: Chromium; Nickel; Electrocoagulation; Copper electrodes; Heavy metals; SEM

1. Introduction

Heavy metals—that is, elements with high atomic weights and a specific gravity greater than five—can contaminate wastewater [1]. Direct and indirect discharge of wastewater containing heavy metals into the environment has increased, especially in developing countries. The industrial activities that are the main sources of heavy metals include the production of fertilizer, batteries, paper, and pesticides; mining; metal plating; and tanneries. Heavy metals are non-biodegradable and can accumulate in living organisms, and several heavy metal ions are both carcinogenic and toxic. Zinc, nickel, copper, cadmium, mercury, chromium, and lead are among the toxic heavy metals that can be found in industrial wastewaters [2]. Nickel (Ni) and hexavalent chromium (Cr(VI)) have poisonous and carcinogenic effects on health; they are usually found in wastewater that results from electroplating industries. Ni is a heavy metal frequently responsible for allergic skin reactions and is one of the most commonly reported causes of allergic contact dermatitis [3]. Cr(VI) is toxic and can cause liver and kidney damage, as well as internal hemorrhaging and the onset of respiratory disorders [4].

Electrochemical wastewater treatment technologies have been found to be promising, especially for the removal of heavy metals; these technologies are environmentally friendly, produce low amounts of sludge, and require a minimal footprint with no addition of chemicals [5,6]. Electrocoagulation and electroflotation can replace conventional coagulation and flotation processes in wastewater treatment plants. In the electrocoagulation (EC) process, sacrificial anodes are dissolved when connected to a current source, producing active coagulants [7]. This technology combines the benefits of coagulation, flotation, and electrochemistry [8]. The advantages of EC compared to chemical

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coagulation can be summarized as follows: simple equipment is used that is easy to operate, the wastewater treated using EC is less turbid, it results in colorless and odorless water, and the sludge produced during the EC process has better settling and dewatering characteristics [9,10]. During the EC process, the flocs produced are usually larger than those produced in chemical coagulation, they include less bound water, and are more stable and acid resistant, which improves the ease with which they can be separated by filtration. EC effluent also contains less dissolved solids in total than chemical treatment effluents do, which reduces the cost of water recovery when this water is reused [11].

Copper (Cu) electrodes were used in a previous study for the removal of arsenite at initial arsenite concentrations of 2.0–25.0 mg/L. The maximum removal of arsenite that was achieved was 99.56%, which occurred at lower initial concentrations [12]. Cu electrodes have also been studied in the removal of chemical oxygen demand (COD) from printing wastewater; COD removal reached 67%, obtained at a current density (CD) of 28 mA/cm^2 [8]. For the treatment of rice grain-based distillery effluent, EC with Cu electrodes, at a CD of 89.3 A/m^2 and a pH of 3.5, was found to be optimal; this process provided a maximum COD and color removal of 80% and 65%, respectively [13]. Cu electrodes were also studied for the treatment of distillery spent wash, where a current intensity of 1.5 A, a dilution of 10%, and an electrolysis time of 5 h, were found to make up the optimal conditions; the treatment yielded a maximum of 77.11% color removal [14]. Ni and Cr uptake from metal plating wastewater, by the process of EC, was studied using four different electrode combinations at different pH values (from 3.0 to 9.0). Efficiencies of the removal of Cr ranged from 91.1% to 95.1% for an iron electrode, or 82.7% to 93.5% for an aluminum electrode, after 10 min of EC. Efficiencies of the removal of Ni ranged from 76.9% to 99.3% for the iron electrode, or 84.9% to 99.1% for the aluminum electrode, after 30 min of EC. Across the different electrode pairs, Ni concentrations in effluent were minimal at a pH of 9.0 [15]. Another study of Ni and Cr removal from the electroplating industry's wastewater conducted depollution tests; two voltages, 6 and 12 V, were applied to aluminum electrodes and their performance was evaluated. The abatement rates determined for Ni and Cr using 6 V reached 63% and 42%, respectively, while the rates using 12 V reached 88% and 66% [16]. Another work upon simulated wastewater studied the effects of different parameters—such as initial pH (2–10), electrolysis time (5–30 min), current density (CD) (0.075–0.186 A/cm^2), initial ion concentration (50–250 mg/L), inter-electrode distance (3–6 cm), and temperature (30°C–70°C)—on the removal efficiencies for metal ions. Optimal pH values of 8 (with a removal efficiency of 99%) and 7 (also, 99%) were obtained for Ni and Cr, respectively [17].

At the anode:

$$\mathrm{Cu}_{(s)} \rightarrow \mathrm{Cu}^{2+}_{(aq)} + 2e^{-} \quad (1)$$

At the cathode:

$$2\mathrm{H_2O}_{(l)} + 2e^{-} \rightarrow \mathrm{H}_{2(g)} + 2\mathrm{OH}^{-}_{(aq)} \quad (2)$$

In the solution:

$$\mathrm{Cu}^{2+} + 6\mathrm{H_3O}^{+}_{(aq)} \rightarrow \left[\mathrm{Cu}\left(\mathrm{H_2O}\right)_6\right]^{2+}_{(aq)} + 6\mathrm{H}^{+}_{(aq)} \quad (3)$$

$$\left[\mathrm{Cu}\left(\mathrm{H_2O}\right)_6\right]^{2+}_{(aq)} + 2\mathrm{OH}^{-}_{(aq)} \rightarrow 6\mathrm{H_2O}_{aq} + \mathrm{Cu}\left(\mathrm{OH}\right)_{2(s)} \quad (4)$$

Overall reaction:

$$\mathrm{Cu}_{(s)} + 2\mathrm{H_2O}_{(l)} \rightarrow \mathrm{Cu}\left(\mathrm{OH}\right)_{2(s)} + \mathrm{H}_{2(g)} \quad (5)$$

According to the author's knowledge, the removal of Ni and Cr(VI) via EC using Cu electrodes has not yet been investigated. Thus, the aim of this research is to study the performance of the EC process using Cu electrodes, through batch and continuous modes of operation, in order to treat synthetic and real wastewater containing Ni and Cr(VI). The research will be conducted under various experimental conditions pertaining to pH, CD, electrolysis time, the spacing between electrodes, and electrolyte type. Chemical coagulation using Cu salts will also be performed, in order to compare its results with those of the EC. Finally, energy consumption for the EC cell will be estimated.

2. Material and methods

2.1. Wastewater characteristics

Nickel nitrate (96.0% purity, Chem-Lab NV) and potassium dichromate (99.5% purity, LOBA Chemie) were used to prepare synthetic wastewater solutions with concentrations of 100 ppm. Sodium chloride (NaCl) (99.8% purity CHEM-LAB) and magnesium chloride ($\mathrm{MgCl_2}$) (98.0% purity, Qualikems) were used to prepare electrolyte solutions with concentrations of 1,000 ppm. Hydrochloric acid (HCl) (36.0% purity, ADVENT) and sodium hydroxide (NaOH) (98.0% purity, ADVENT) were used for pH adjustment. For the set of experiments using real wastewater, the real wastewater was obtained from the outlet of the primary sedimentation tank at the Aburawash treatment plant, Giza, Egypt; its characteristics are shown in Table 1. Ni and Cr(VI) salts were added to reach concentrations of 100 ppm. For the chemical coagulation experiments, copper sulfate ($\mathrm{CuSO_4}$) (98.5% purity, LOBA Chemie) was used to compare the performance of EC using Cu electrodes with that of chemical coagulation.

Table 1
Characteristics of real wastewater

Characteristics	Value	Unit
COD	150	ppm
TSS	120	ppm
TDS	700	ppm
Ni	100	ppm
Cr(VI)	100	ppm
Conductivity	970	µs/cm
pH	6.8	–
Temperature	28	°C

2.2. Electrocoagulation system setup

Experiments were conducted in an EC cell consisting of a 500 mL glass beaker that contained two electrodes, fixed vertically and parallel to each other, as shown in Fig. 1. The anode used was Cu and the cathode was stainless steel. The electrode dimensions were 10 cm × 4 cm; thus, the electrode surface area was 80 cm^2 per plate (double-sided). The distances of the gaps studied between electrodes were 2, 4, and 6 cm. The electrodes were connected to a laboratory DC power source (Velleman ENERGY LABPS3005SM) set to direct current mode in all experiments. Synthetic wastewater was treated at room temperature with different applied CDs (5, 10, and 15 mA/cm^2), for different reaction times (1, 5, 10, 15, 30, 45, 60, and 90 min), with different initial pH values (acidic, neutral, and basic), and using two types of electrolytes (NaCl and $MgCl_2$). After each EC run, the water was allowed to settle for 45 min, and then water samples were filtered through a filter paper, in order to simulate both particle separation by sedimentation and filtration using a vacuum pump. A magnetic stirrer was used at 100 rpm to mix the beaker's contents. The same process was repeated using real wastewater, with Ni and Cr added separately and combined at the optimal conditions, without adjusting the initial pH and with no salt added. Electrodes were washed with 4% HCl and tap water after each experiment.

For the continuous mode of operation, experiments were conducted in a 500 mL glass beaker that was continuously fed with wastewater from a tank placed at a high elevation, through a pipe tube with a 1 cm diameter. The beaker was equipped with a valve that was opened partially to ensure that wastewater left the beaker at the designated flowrate. These experiments used the real wastewater with combined additions of Ni and Cr(VI); they were conducted at room temperature under the optimal conditions determined from the previous experiments. Finally, samples were taken at 10 min intervals to measure the Ni and Cr(VI) removal efficiencies.

Chemical coagulation tests were conducted with jar test apparatus. $CuSO_4$ was used as the coagulant to simulate the flocs formed from Cu electrodes in EC. Conventional coagulation experiments were conducted as follows: rapid mixing for 1.5 min at 100 rpm, followed by gentle mixing for 20 min at 30 rpm, then 20 min for sedimentation, and finally samples were collected for analysis [8].

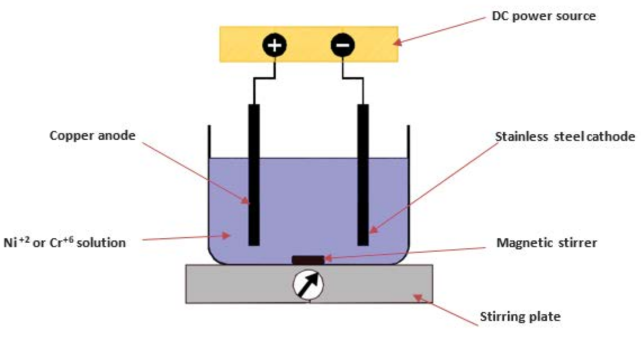

Fig. 1. EC cell setup.

2.3. Analysis

Samples of influent and effluent were collected for analysis at the designated time intervals. Ni and Cr(VI) final concentrations were measured using atomic adsorption spectroscopy (Thermo Scientific, iCE 3000 series, ThermoFisher, USA). The pH was measured using an inoLab pH 720 pH meter (WTW Series). The efficiency of removal of the contaminant (R) after processing was calculated as in Eq. (6):

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \tag{6}$$

In this equation, C_0 is the initial concentration of the pollutant and C_e is the final concentration of the pollutant. The current efficiency was calculated using Eq. (7) [18]:

$$\phi = \frac{m \times z \times f}{M \times I \times t} \times 100 \tag{7}$$

In this equation, ϕ is the current efficiency (%); m is the electrode mass lost at the end of the EC process (g); z is the number of electrons transferred in the electrode reaction (for Cu, $z = 2$); f is the Faraday's constant (96,486 C/mol); M is the atomic weight of copper (gm/mol), I is the current passed (A); and t is the time duration of the EC experiments. The morphologies of the Cu electrodes were investigated using scanning electron microscopy (SEM) at the National Research Center (Model: Quanta FEG 250, FEI). The experiments were conducted in duplicate, and the results are shown in the following section present the average values of these measurements.

3. Results and discussion

3.1. Effect of initial pH

The effect of initial pH value was studied at a CD of 10 mA/cm^2 and an electrode spacing of 4 cm, using NaCl salt. The maximum removal efficiency of Ni reached 99.96% at an initial pH of 9.2 and an electrolysis time of 90 min, as shown in Fig. 2. During the first 10 min, the rate of Ni removal for all pH values was high; then, the rate of removal decreased as the oxidation reactions that promote the corrosion of the electrode led to the formation of stable oxide layers on the surface of the anode electrodes. These layers cause passivation effects that decrease the efficiency of the EC cell [8]. On the other hand, the high solubility of Cu ions in basic conditions (i.e., pH = 9.2) causes the formation of Cu oxides; these act as a coagulant to adsorb the pollutant (Ni), forming complexes and leading to its removal by settling and flotation. It is worth noting that a 99.42% removal was reached after only 15 min of the reaction time, which is beneficial for reducing the energy consumption of the setup. The same behavior was observed for other pH values. At an initial pH of 6.8, the removal rate increased rapidly during the first 10 min and the removal efficiency reached 79%; then, the removal rate decreased and the removal efficiency reached approximately 99.9% in the end. At an initial pH of 2.7, the removal rate increased rapidly during the first 15 min and the removal efficiency reached 96.4%; then, the removal rate decreased and the removal efficiency reached approximately 99.9%.

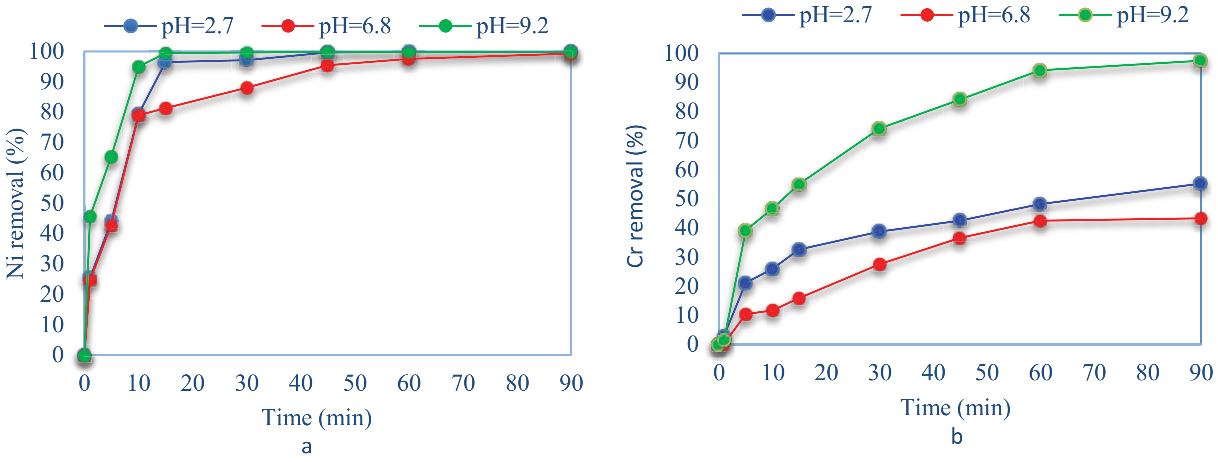

Fig. 2. Ni and Cr(VI) removal efficiencies at various initial pH values: (a) Ni removal and (b) Cr(VI) removal.

With regards to Cr, the maximum removal was 97.5%, which was obtained with an initial pH of 9.2 and an electrolysis time of 90 min. The removal rate was observed to increase rapidly for the first 60 min, then the rate started decreasing. Removal at neutral and acidic pH values was much lower than in the basic range, unlike in the case of Ni removal; it reached only 55.3% in the acidic pH range and 43.4% in the neutral range by the end of the reaction time.

The pH also increased during the reaction, as shown in Fig. 3. For both Ni and Cr, for all initial pH values, the final pH reached 11.7 by the end of the experiment. The pH increased because hydroxide groups tend to form metal hydroxide flocs, and when an OH^- group concentration increases, an H^+ group concentration decreases, leading to an increase in pH values towards the end of the reaction time.

3.2. Effect of current density

The rate of Ni removal for all CDs increased rapidly during the first 10 min; then, the rate of removal of Ni decreased. The best removal efficiency of Ni was 99.96%, obtained at CD = 10 mA/cm^2, and was reached after 90 min. An efficiency of 99.42% was reached in only 15 min, as shown in Fig. 4. The rate of anode dissolution increased with the CD. This led to the production of a higher number of metal hydroxide flocs, resulting in a higher removal efficiency. Increasing the CD above the optimal value did not cause a further increase in the efficiency of removal of the contaminant. This is because, at the optimal value, sufficient numbers of metal hydroxide flocs were available for the sedimentation of the contaminant [11]. It was also noted that the EC cell could be operated for just 15 min, because the removal efficiency after 90 min was only slightly higher than that after 15 min. This shorter reaction time would reduce the power consumed by the process. At CD = 5 mA/cm^2, the removal efficiency was also satisfactory; it reached a maximum removal of 97.2% after 45 min, which reduces power consumption. At CD = 15 mA/cm^2, removal reached 98% after 60 min, which is almost the same performance as with lower CDs.

Cr removal exhibited a different pattern than Ni; the maximum removal efficiency of Cr was 98%, which was obtained at CD = 5 mA/cm^2 at the end of the experiment. At CD = 5 mA/cm^2, the rate of removal was observed to increase quickly during the first 10 min; then, the rate of removal efficiency of Cr decreased. In contrast, other CDs did not produce this rapid Cr removal. It was also noted that EC for Cr removal did not require 90 min, as it reached a high level of removal (88%) after only 10 min at a low CD. At CD = 10 mA/cm^2, the maximum removal was 97.5% after

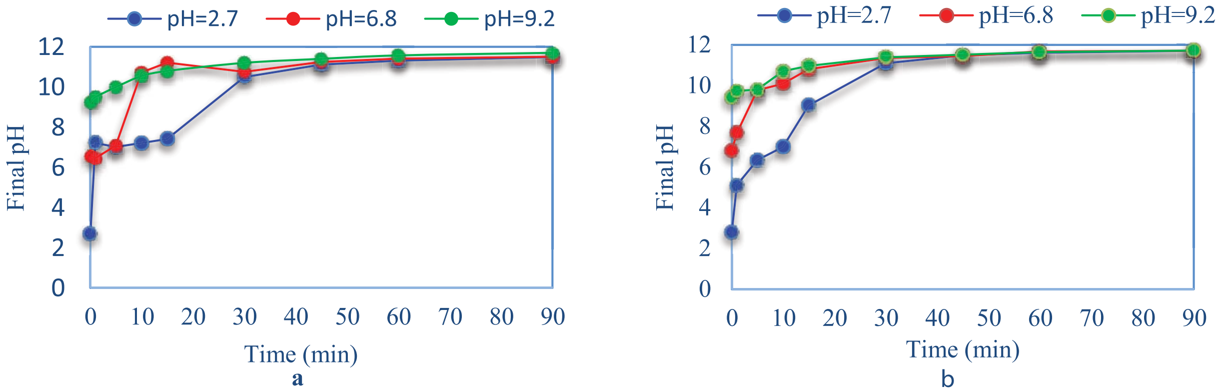

Fig. 3. Change in pH over time for various initial pHs: (a) Ni removal and (b) Cr(VI) removal.

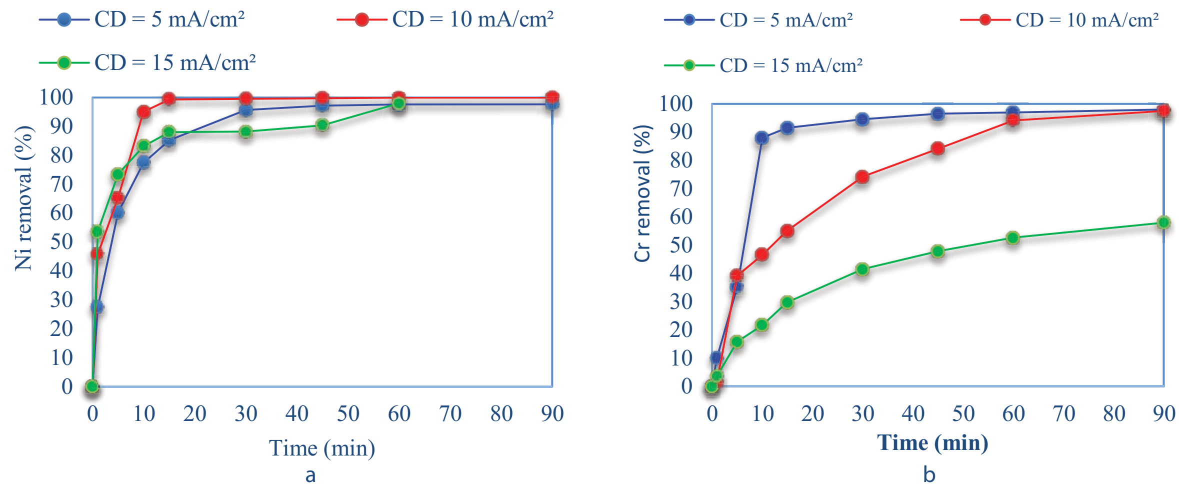

Fig. 4. Ni and Cr(VI) removal efficiencies at various CDs: (a) Ni removal and (b) Cr(VI) removal.

90 min; at CD = 15 mA/cm², it reached 57.95% after 90 min, which is low for removal when compared with other CDs.

3.3. Effect of electrodes' spacing

As shown in Fig. 5, different electrodes' spacings were studied (2, 4, and 6 cm). The removal pattern for Ni was almost the same for all spacings; after 90 min it reached 97.6%, 99.96%, and 92% at gaps with distances of 2, 4, and 6 cm, respectively. The removal rate of Ni was high for the first 10 min, which means that shorter reaction times can be used. The behavior during the removal of Cr was different; the removal rates at 2 and 6 cm were remarkably lower than at 4 cm. The maximum efficiency of 98% was obtained under the following experimental conditions: spacing = 4 cm, time = 90 min, pH = 9.2, CD = 5 mA/cm², and using NaCl salt. At gaps with distances of 2 or 6 cm, the Cr removal efficiencies decreased sharply when compared with those at the 4 cm spacing (with a 34% removal at 2 cm spacing and a 39% removal at 6 cm spacing by the end of the reaction time). The distance between electrodes had a significant effect on the EC cell performance, as the electrostatic field was dependent upon this distance. Maintaining an optimal distance between the electrodes resulted in a higher removal efficiency. The pollutant removal efficiency was low at a less-than-optimal distance between electrodes, because the metal hydroxide flocs that are generated are degraded by collisions with each other, which are caused by a high electrostatic attraction force. Increasing the distance between electrodes to the optimal value leads to an increase in the removal efficiency because it decreases the electrostatic effects and results in slower movement of the ions that are generated. This allows more time for the metal hydroxide that is produced to agglomerate and form flocs, leading to increase in pollutant removal. When the electrode spacing is increased to a more-than-optimal distance, a reduction in the efficiency of pollutant removal is observed, because the travel time of the ions increases. This increase is brought about due to a decrease in the electrostatic attraction, leading to a decrease in the formation of the flocs that are needed to coagulate the pollutant [11].

3.4. Effect of electrolyte type

As shown in Fig. 6, using NaCl salt as the electrolyte resulted in a better performing EC process, than when using $MgCl_2$. When using NaCl salt over a reaction time of 90 min (at pH = 9.2, CD = 10 mA/cm², and electrode spacing = 4 cm),

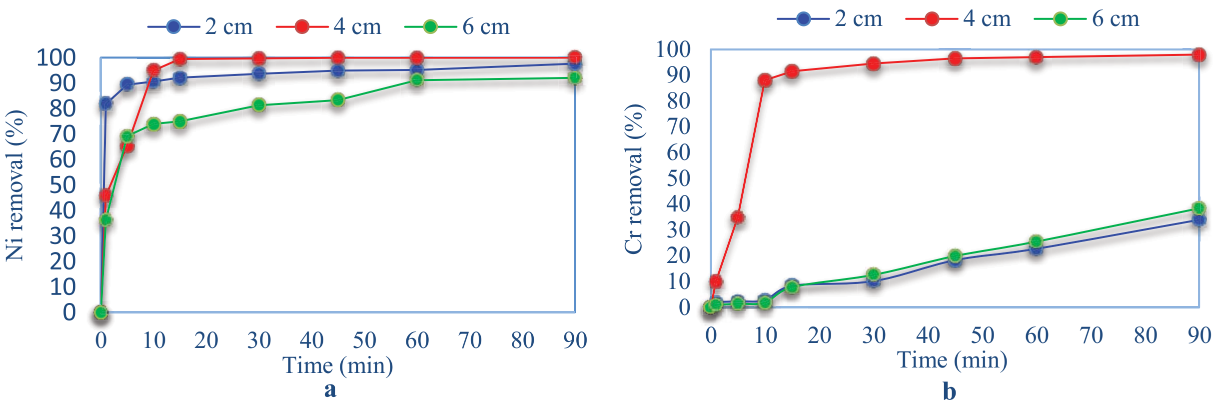

Fig. 5. Ni and Cr(VI) removal efficiencies at various electrode spacings: (a) Ni removal and (b) Cr(VI) removal.

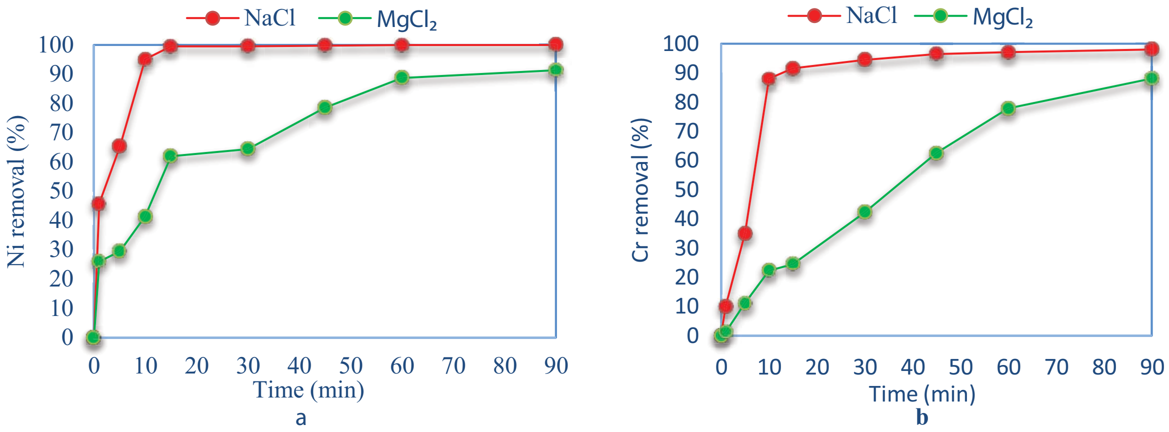

Fig. 6. Ni and Cr(VI) removal efficiencies using two electrolyte types: (a) Ni removal and (b) Cr(VI) removal.

the removal efficiency of Ni reached 99.96% and the current efficiency reached 70%. As can be observed, the rate of Ni removal increased rapidly during the first 10 min when NaCl salt was used as the electrolyte; then, the rate of the removal efficiency of Ni decreased. For $MgCl_2$, rapid removal of Ni was observed immediately after 1 min; then, removal reached 62% after 15 min, going on to reach 91.35% at the end of the experiment (at pH = 9.2, CD = 5 mA/cm^2, and spacing = 4 cm). For Cr, a maximum removal efficiency was observed to be 98%, along with a current efficiency of 60%; these results were obtained using NaCl salt, in a reaction time of 90 min. In that case, the rate of Cr removal increased rapidly during the first 10 min; then, the rate of removal efficiency of Cr decreased. For $MgCl_2$, the maximum removal efficiency of Cr was observed to be 88% at the end of the experiment. Thus, the optimal salt type for Cr removal was NaCl. When comparing the ionization energies of the two atoms, the ionization energy of Na is 496 kJ/mol while the first ionization energy of Mg is 734 kJ/mol. Thus, Na ionizes more readily than Mg, since the anion (chloride) is the same in both cases.

3.5. Real wastewater

Real wastewater, with either Ni or Cr(VI) added, was treated based on the optimal conditions that were previously determined (CD = 10 mA/cm^2, electrode spacing = 4 cm, and no salt addition); that is, all except for pH, which was left at its original value (pH = 6.8). The maximum removal efficiency of Ni was observed to be 99.4%, obtained at a reaction time of 90 min as shown in Fig. 7. Most Ni removal was achieved in the first 30 min; then, the rate of removal efficiency of Ni became nearly constant. The removal efficiency was slightly lower than in synthetic wastewater, due to the competition of other pollutants with Ni [10].

At pH = 6.8 (no pH adjustment), CD = 5 mA/cm^2, spacing = 4 cm, and with no salt added, the maximum removal efficiency of Cr was 65%, obtained at a reaction time of 90 min. Cr also exhibited a lower removal efficiency in real wastewater than in synthetic wastewater, due to the competition of other pollutants with Cr(VI) and because the pH of the real wastewater was not in the basic range.

Real wastewater, containing both heavy metals, was also treated based on the previously determined optimal conditions, that is, pH = 6.8 (no pH adjustment), CD = 10 mA/cm^2, and spacing = 4 cm, with no salt added. The maximum removal efficiencies of Ni and Cr were 99.6% and 91.68%, respectively, which were obtained at a reaction time of 90 min, as shown in Fig. 8. It is obvious that the combination of both pollutants slightly affects Ni removal, due to internal reactions in the presence of Cr(VI). On the other hand, Cr(VI) removal decreased due to the effects of Ni.

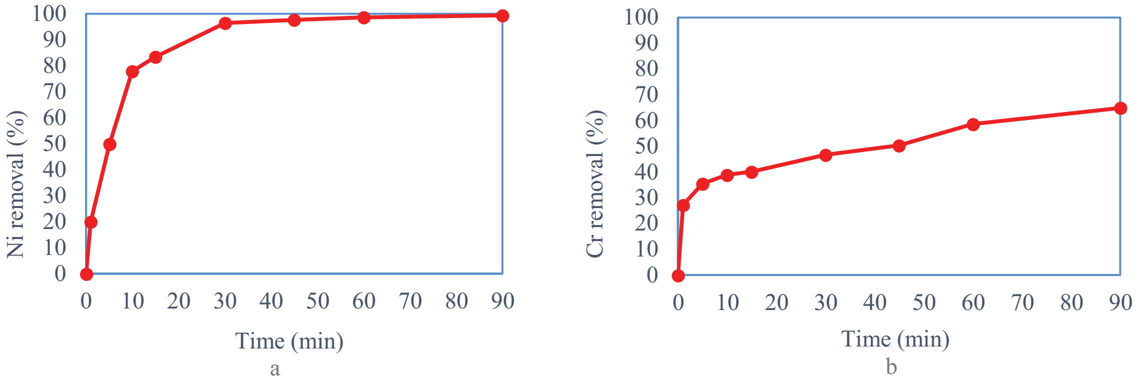

Fig. 7. Ni and Cr(VI) removal as a function of electrocoagulation time (pH = 6.8, CD = 10 mA/cm^2, and electrode spacing = 4 cm).

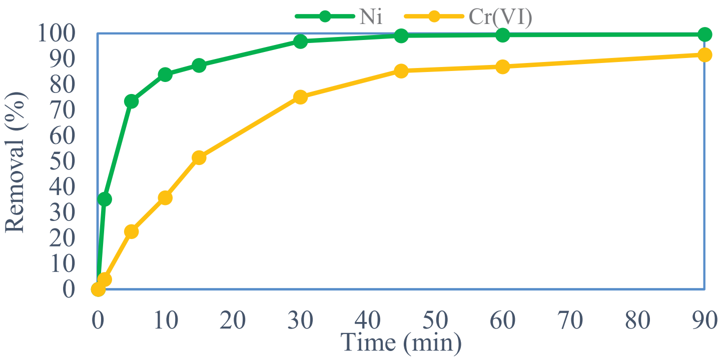

Fig. 8. Ni and Cr(VI) removal as a function of electrocoagulation time (pH = 6.8, CD = 10 mA/cm^2, and electrode spacing = 4 cm, batch mode).

EC was operated in continuous mode (at pH = 6.8, CD = 10 mA/cm^2, electrode spacing = 4 cm, and with no salt added), in order to examine its potential for practical use. The removal of Ni and Cr, from real wastewater containing both heavy metals, occurred at an efficiency of 98.5% and 59.2%, respectively, in a time of 30 min. COD removal efficiency was also calculated and reached 50%. Batch mode creates higher removal efficiencies when compared with continuous mode; this can be related to the stability of flocs in the batch mode, where they are not disturbed (compared with the continuous mode, where the flow regime can break flocs).

3.6. Morphology of electrodes

The morphologies of the electrodes were studied before and after their introduction in the EC cell, at optimal operating conditions, as shown in Fig. 9. Corrosion

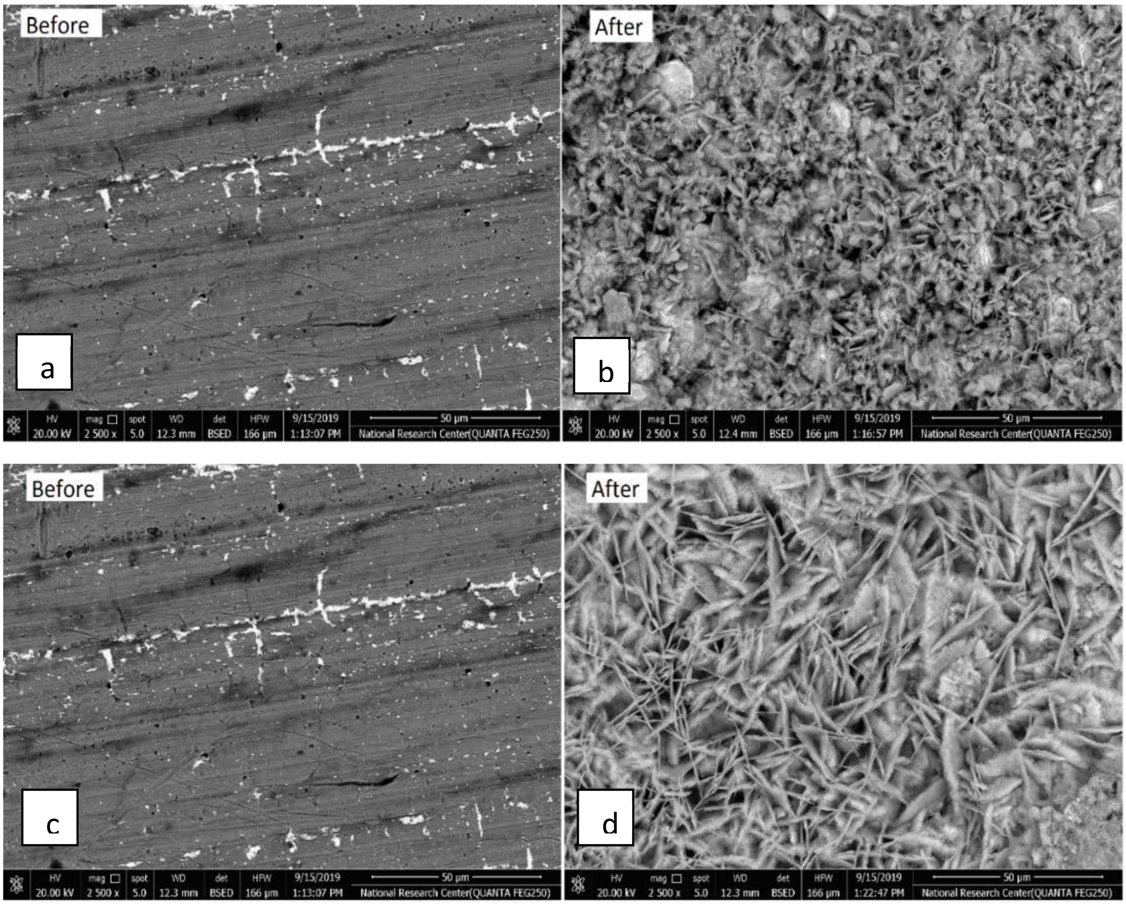

Fig. 9. SEM images of Cu electrodes: (a) Cu electrode before treatment in case of Ni removal, (b) Cu electrode after treatment in case of Ni removal, (c) Cu electrode before treatment in case of Cr(VI) removal, and (d) Cu electrode after treatment in case of Cr(VI) removal.

was observed on the electrodes' surfaces, which is indicative of their dissolution during the treatment process. The surface of the Cu anode showed a large number of cracks and dents; this indicates the consumption of metal at active sites. Corrosion on the Cu electrode was uniform [8].

3.7. Chemical coagulation

$CuSO_4$ was used at different coagulant dosages, in order to investigate Ni and Cr(VI) removal via chemical coagulation, for the purpose of comparison with EC. Jar test apparatus was used at five different coagulant doses (2, 10, 20, 30, and 40 g/L), as shown in Figs. 10 and 11. The maximum removal efficiencies for Ni and Cr(VI) were 17% and 16.4%, respectively, at the highest coagulant dose. These removal values were much lower than those of EC, although the coagulant dose that was used was high (40 g/L). During the EC process, the flocs produced are usually larger than those produced in chemical coagulation, include less bound water, and are more stable; this leads to a higher removal efficiency for EC, due to the EC floc's ability to adsorb more particles of pollutant than that of chemical coagulation [11]. According to these results, it can be concluded that EC performs better at removing heavy metal from wastewater than chemical coagulation does.

3.8. Electrical energy consumption

The electrical energy consumed in the treatment of the real wastewater was plotted vs. the operating time at different CDs, as shown in Fig. 12. The electrical energy consumption (EEC, kWh/m^3) was calculated according to Eq. (8):

$$\mathrm{EEC} = \frac{UIt}{1{,}000V} \tag{8}$$

In this equation, U is the applied voltage (V), I is the electrical current (A), t is the EC time (h), and V is the volume of treated water (m^3). The results show that energy consumption increased with reaction time. The maximum energy consumption values were 23.7 and 24.7 kWh/m^3 for Ni and Cr(VI) removal, respectively. These values are in accordance with values found in the literature for the electrical energy consumption of EC processes, ranging from 34 to 40 kWh/m^3 [19].

For Ni and Cr(VI) removal, from real combined wastewater at an initial pH of 6.8, the EEC was 30 kWh/m^3 at the end of the reaction time, as shown in Fig. 13.

3.9. Cost analysis

To evaluate whether a proposed wastewater treatment system could be applied at commercial scales, its operating cost should be included as a factor in the optimization procedure. The operating costs of the EC reactor, as US$ m^{-3} of treated effluent, should include the consumption of two main items: energy and electrode material. The electrical operating cost (EOC) is the electrical energy consumed, as kWh/m^3 of treated effluent, multiplied by the electrical energy price (EEP), as US$/kWh. The EOC can be calculated as shown in Eq. (9):

$$\mathrm{EOC} = \frac{V \times i \times A_e \times t}{V_{\mathrm{eff}}} \times \mathrm{EEP} \tag{9}$$

In Eq. (9), EOC is the electrical operating cost (US$$m^{-3}$), V_{eff} is the total volume of treated effluent (m^3), i is the current density (A cm^{-2}), t is the operating time (h), A_e is the effective superficial area (cm^2), V is the applied voltage (V), and EEP is the electrical energy price (US$/kWh). As for the material cost (MC), this takes into account the maximum possible mass of Cu that could theoretically be dissolved by the anode, using Faraday's law, per m^3 of treated effluent and with the EMP as US$/kg of Cu. The MC parameter can be calculated as shown in Eq. (10):

$$\mathrm{MC} = \frac{M \times i \times A_e \times t}{V_{\mathrm{eff}} \times n \times f} \times \mathrm{EMP} \tag{10}$$

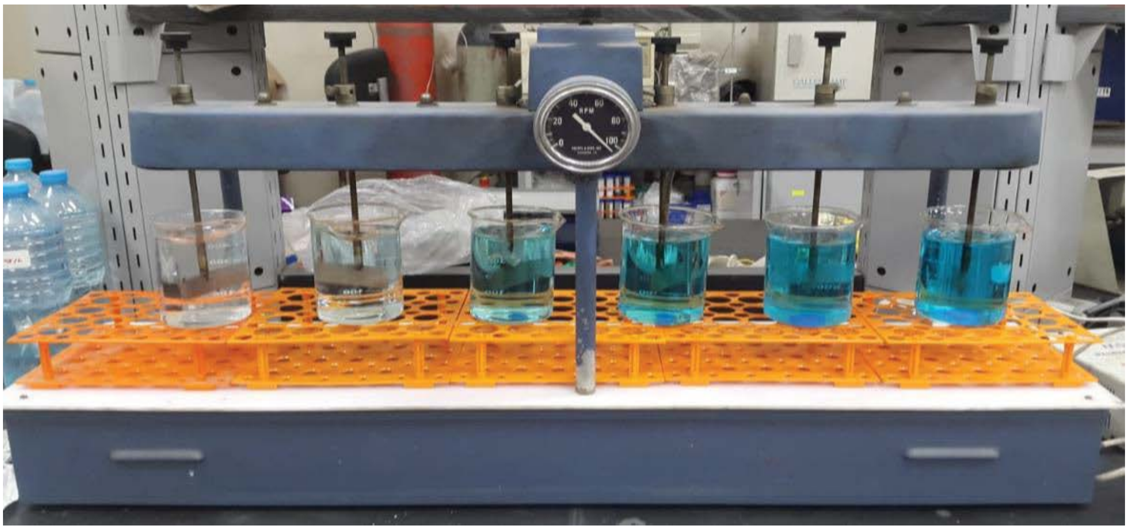

Fig. 10. Jar test using copper sulfate.

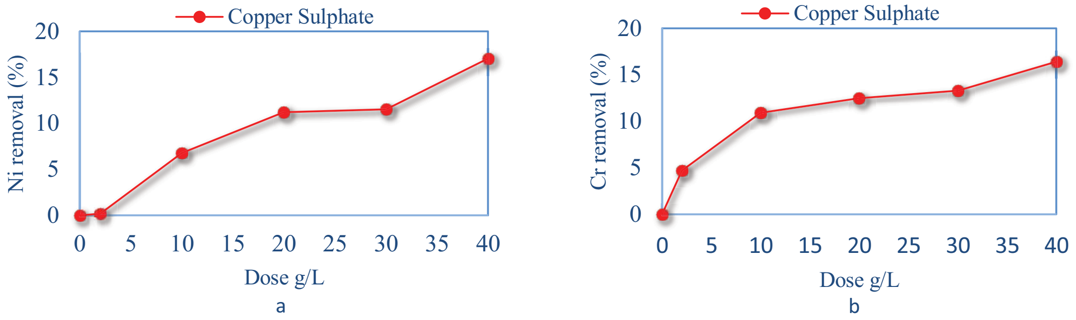

Fig. 11. Ni and Cr(VI) removal efficiencies over different coagulant doses: (a) Ni removal and (b) Cr(VI) removal.

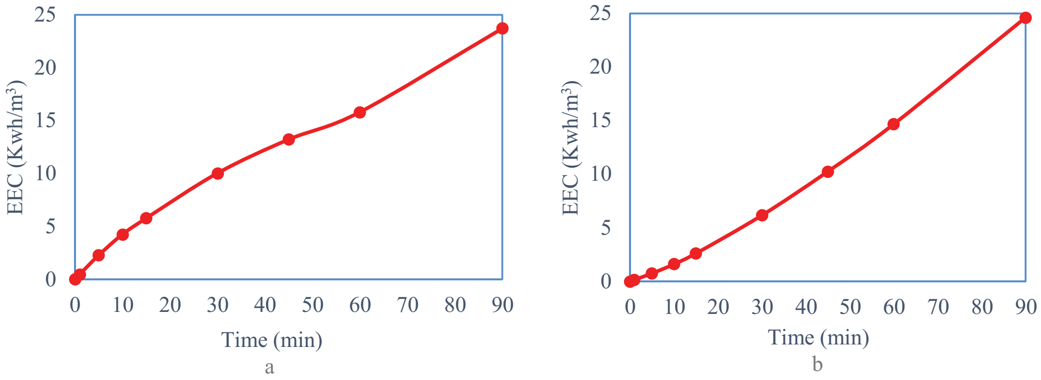

Fig. 12. EEC over time for treatment of real wastewater at optimal conditions: (a) Ni removal and (b) Cr(VI) removal.

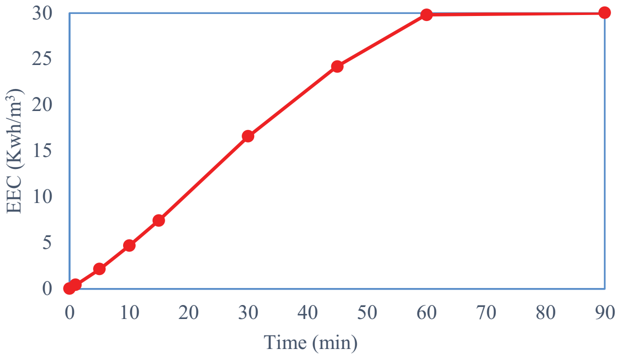

Fig. 13. EEC values as a function of electrocoagulation time (current density = 10 mA/cm^2, Ni, and Cr(VI) removal).

In Eq. (10), MC is the material cost (US\$m^{-3}), M is the relative molar mass of the concerned electrode (g/mol), f is Faraday's constant (96,500 C/mol), EMP is the price of the electrode material (US\$/g), and n is the number of electrons in oxidation/reduction reaction [20]. The price of 1 kWh is 0.1 US\$ and the estimated EEC varies from 0.8–3 US\$/m^3, while the MC is 0.003 US\$/m^3; this leads to a total operating cost of 0.803–3.03 US\$/m^3. The energy consumption values are in accordance with the values obtained for Fe electrodes 2.78 US\$/m^3 for Ni removal, while they are lower than those obtained for Ni removal using Al electrodes, at 9.44 US\$/m^3 [21]. Another study has shown that for Cr and Ni removals using Fe electrodes, the OC were found to be 5.92 and 10.47 US\$/m^3, respectively [22].

3.10. Comparison with other research work

The results of this study have been compared with previous studies, as is shown in Table 2. It has been found that maximum removal efficiencies are achieved after 90 min. In the case of Ni removal, the removal exceeds 90% after 30 min, which is considered to be sufficient and leads to lower energy consumption and cost if the processing time is reduced accordingly. As shown in Table 2, the cost of this study has been lower than that of the other studies with which its results can be compared.

4. Conclusion

This study has proven the ability of EC for the removal of Ni and Cr from an aqueous solution, using copper electrodes. The removal efficiencies have been shown to increase along with an increasing pH until it reaches 9.2. The best removal efficiency reached 99.96% for Ni, at CD = 10 mA/cm^2, while it reached 98% for Cr, at CD = 5 mA/cm^2. The removal pattern for Ni was almost the same for all distances of gaps between electrodes, while the best distance for Cr was discovered to be 4 cm. The removal efficiencies of both Ni and Cr were higher when using NaCl as an electrolyte, compared with $MgCl_2$. When using real wastewater, the removal efficiencies of both Ni and Cr were

Table 2
Comparison between results of this study and previous studies

Pollutant	Initial concentration (mg/L)	Electrode material	Current density (mA/cm²)	Processing time (min)	pH	Removal (%)	Cost	Reference no.
Cr	358	Fe	30	30	5	98.9	5.34 $/m³	[22]
Ni	8.1	Fe	30	30	5	96.3	10.47 $/m³	[22]
Ni	23.1	Fe	30	16	10	95.22	2.78 $/m³	[21]
Ni	23.1	Al	38	30	10	92.49	9.44 $/m³	[21]
Cr	44.5	Fe–Fe/Fe–Al	10	20	3	100	–	[23]
Ni	394	Fe–Fe/Fe–Al	10	20	3	98	–	[23]
Ni	100	Cu–SS	10	90	6.8	99.40	2.24 $/m³	This study
Cr	100	Cu–SS	5	90	6.8	64.88	2.26 $/m³	This study

lower, due to the competition with other pollutants present in the real wastewater. When treating real wastewater containing both Ni and Cr, the maximum removal efficiencies of Ni and Cr were 99.6% and 91.68%, respectively, obtained after an electrolysis time of 90 min. The batch mode has higher removal efficiencies when compared with the continuous mode. When using SEM to monitor the surface of the electrode used to treat both Ni and Cr, the surface of the Cu anode showed a large number of cracks and dents, indicating the consumption of metal at active sites, while the corrosion in the Cu electrode was uniform. EC was found to perform better than chemical coagulation at removing heavy metal from wastewater. The results show that energy consumption increases with reaction time; the maximum energy consumption values were 23.7 and 24.7 kWh/m³ for Ni and Cr(VI) removal, respectively. The estimated EEC varied from 0.8–3 US$/m³, while the MC was 0.003 US$/m³.

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