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Treatment of Cr, Ni and Zn from galvanic rinsing wastewater by electrocoagulation process using iron electrodes

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ABSTRACT

Galvanizing plants contain reasonable amounts of heavy metal ions which pose a serious risk to humans, animals and the environment. In the present study, removal efficiencies of Cr, Ni and Zn from galvanic rinse wastewater (GRW) by electrocoagulation (EC) process using iron plate electrodes were investigated in a laboratory scale EC reactor. The effects of operational variables, such as operating time (0–50 min), current density (10–40 A/m^2), initial pH$_i$ (2.4–6.4) and electrode connection modes (MP-P: monopolar-parallel, MP-S: monopolar-serial and BP-S: bipolar-serial), on the removal efficiencies of heavy metals were explored to determine the optimum operating conditions. Removal efficiencies of 99.77% for Cr, 85.62% for Ni and 99.04% for Zn at the optimum operating conditions (pH$_i$ 5.4, current density of 30 A/m^2, operating time of 30 min and MP-P electrode connection mode) were obtained. The results showed that Cr, Ni and Zn removal efficiencies from GRW increased with increasing current density and pH at MP-P electrode connection mode. The results showed that EC can effectively reduce metal ions to a very low level. Amount of sludge generated and operating cost at the optimum conditions during the EC process were calculated as 2.32 kg/m^3 and 0.70 €/m^3. This study revealed that the EC process was very effective for removal of Cr, Ni and Zn from GRW.

Keywords: Galvanic rinse wastewater; Electrocoagulation; Operating cost; Iron electrodes; Electrode connection modes

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1. Introduction

Galvanizing operations are widely used in the industry because coating of metal tools with Co, Cr, Ni, Zn, etc. can improve mechanical and chemical properties, such as hardness, toughness and corrosion resistance [1]. Galvanizing plants have been identified as an environmental risky industrial sector concerning the potential hazardous nature of its own waste streams, since they often contain reasonable amounts of metals [2]. A galvanic process consists of a metal plating bath, where a work piece is plated, followed by a rinse system that usually consists of a series of rinse tanks [3]. Rinsing waters become contaminated

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during the plating process due to “drag-out” from the previous plating baths. The contaminated rinse wastewaters may contain heavy metals, such as chromium, copper, zinc, lead, nickel and iron, depending on the plating process. Consequently, the rinse wastewaters are major causes of water and soil pollution. Heavy metals in these wastewaters pose a serious risk to humans, animals and the environment. Therefore, it is necessary to treat them before being discharged into the environment.

Spent rinsing wastewaters were treated by some treatment techniques, such as coagulation–flocculation, adsorption, ion exchange, solvent extraction, membrane filtration and reverse osmosis, to produce effluent concentrations that meet standards for discharge to the sewage system [4–6]. However, the above methods still did have their own limitations during the treatment because of the generation of a large amount of secondary waste products and high operating costs. Moreover, removal of toxic metals from galvanic wastewater by conventional techniques was carried out by precipitation as hydroxides with lime or caustic, such as copper, nickel, and zinc, and afterwards sedimented or filtered [7]. Unlike many other metals, Cr(VI) in galvanic wastewater must be reduced to the trivalent state Cr(III) for preceding the precipitation process. The most common method used was acidic reduction (pH 2–3) with chemicals namely, sulphur dioxide, sodium sulphite or sodium bisulphate [8]. After chromium reduction, the pH must be raised to 9–10 to precipitate all metals effectively. This was achieved with lime, sodium hydroxide or magnesium hydroxide. Thus, Cr(III) and other metals were precipitated or co-precipitated as hydroxides and separated from solution by sedimentation or filtration. Although acidic reduction with subsequent precipitation was shown to be quite efficient in treating industrial effluents, chemical coagulation may induce secondary pollution caused by high amounts of added chemical substances.

The disadvantages encouraged many studies to use electrocoagulation (EC) processes for the treatment of several industrial effluents, such as electroplating processes [9–14]. EC is a process consisting of generating metallic hydroxide flocs within the water by electrodissolution of sacrificial metal electrodes. The EC process does not require any supplementary addition of chemicals, reduces the volume of produced sludge and is cost-effective as compared to the conventional methods. Recently, the EC process was employed for the removal of metals, such as Cu, Cr and Ni, from a metal plating wastewater with Fe–Fe and Fe–Al plate electrode pairs [10]; Ni, Cu and Cr from a galvanic wastewater with Fe and Al electrodes [12]; Ni and Cd from an electroplating rinse water with Fe electrode [13]; Cu, Pb and Cd from a synthetic wastewater with Fe plate electrode [14]; Cu from a copper polishing wastewater with Al–Fe electrodes [15]; Mn from a synthetic wastewater with Al plate electrode [16]; Hg from a synthetic wastewater with Fe and Al plate electrodes [17]; Ni and Zn from a metal plating wastewater using steel electrodes [18], and other similar studies [19–27]. Table 1 also provides an overview of EC studies performed in the literature with real and synthetic wastewaters containing heavy metals.

In this study, the removal of Cr, Ni and Zn from galvanic rinse wastewater (GRW) by EC process using iron plate electrodes was investigated. The effects of operational variables, such as operating time, current density, electrode connection mode and initial pH, on the removal efficiencies of metals from the wastewater were explored to determine the optimum operational conditions and operating cost of the EC process. The effects of those parameters were investigated to enhance the EC process performance.

2. Materials and methods

2.1. Characteristics of GRW

GRW was obtained from a local electroplating factory located in Istanbul, Turkey. The wastewater was stored in a 60 L high-density polyethylene container at 4°C and was analysed with standard analytical methods [28]. Characterizations of GRW were depicted in Table 2.

2.2. EC reactor and experimental procedure

The EC experiments were conducted in a batch process using a 1,000 mL capacity EC reactor constructed from Plexiglas having a dimension of $12 \times 11 \times 11$ cm. Iron (Fe) plates (purity > 99.5%) with dimensions of $5 \times 7.3 \times 0.3$ cm, were used for the sacrificial electrodes. In each batch, four Fe plate electrodes, two anodes and two cathodes, positioned vertically and spaced by 1 cm, were placed in the EC reactor. The influence of the distance between the electrodes on the efficiency of the process might be explained by the fact that the electrostatic field which depends on the distance between the electrodes diminishes as this parameter increases. A low field might result in a slower displacement of the ions formed during the electrolysis and then facilitates their flocculation, which renders the binding of metal ions in solution by iron hydroxide more efficiently. The total effective electrode area was 219 cm^2. Before each run, the impurities on the Fe electrode surfaces

Table 1
An overview of literature studies with real and synthetic wastewaters containing heavy metals in the EC process

Wastewaters containing metal(s)	Types of EC reactor, electrode and connection mode	Optimum operating conditions and removal efficiency (%)	Ref.
Metal plating wastewater (Cu = 45 mg/L, Cr = 45 mg/L, Ni = 394 mg/L)	Batch reactor, Fe–Fe and Fe–Al plate electrode pairs, $d = 1$ cm (distance between electrodes), MP-P	pH$_i$ 3, $j = 100$ A/m^2, $t_{EC} = 20$ min, Cu = 100, Cr = 100, Ni = 100	[1]
Synthetic wastewater (Cu = 12 mg/L, Pb = 4 mg/L, Cd = 4 mg/L)	Batch and continuous reactors, Fe plate electrode, MP-P	pH$_i$ 7, $j = 36$ A/m^2, $t_{EC} = 10$ min, $d = 2.0$–2.5 cm, Q = 6.3 cm^3/min, Cu = 100, Pb = 100, Cd = 100	[2]
Synthetic wastewater (Cd = 20 mg/L)	Batch reactor; Al, Fe, Mg, and Zn plate electrodes, $d = 0.5$ cm, direct current, MP-P	pH$_i$ 7, $j = 0.2$ A/dm^2, $t_{EC} = 50$ min, Cd = 96.2 (for Al), Cd = 97.3 (for Fe), Cd = 98.6 (for Mg), Cd = 96.9 (for Zn)	[3–6]
Galvanic wastewater (Cr = 98.3 mg/L, Ni = 108.6 mg/L, Zn = 11.3 mg/L, Cu = 1.10 mg/L, pH 3)	Batch reactor, Fe plate electrode, $d = 1$ cm, MP-P	pH$_i$ 6.5, $j = 97.7$ A/m^2, $t_{EC} = 45$ min, Cr = 100, Ni = 100, Zn = 99, Cu = 99, Operating cost = 3.77 \$/m^3	[7]
Galvanic wastewater (Ni = 1,401 mg/L, Cu = 870 mg/L, Cr = 34 mg/L, pH 1.5)	Batch reactor, Combination of Fe and Al electrodes, $d = 2$ cm, BP-S	>pH$_i$ 5, i = 0.2 A (for Fe), i = 1.5 A (for Al), $t_{EC} = 180$ min, Cr = 94, Ni = 95, Cu = 99, pH$_f$ 7.8	[8]
Copper polishing wastewater (Cu = 83 mg/L, COD = 277 mg/L, Turbidity = 180 NTU, pH 7.3)	Batch reactor, Al/Fe electrode pair, $d = 1$ cm, MP-P	$j = 93$ A/m^2 (U = 30 V), $t_{EC} = 30$ min, Cu = 99, COD = 89%, Turbidity = 96 NTU	[9]
Electroplating wastewater (Synthetic: Cu = 50 mg/L, Zn = 50 mg/L, Cr(VI) = 50 mg/L; Real: Cu = 33 mg/L, Zn = 41 mg/L, Cr(VI) = 24 mg/L)	Batch reactor, Al electrode, $d = 0.5$ cm, MP-P	pH$_i$ 6, $j = 480$ A/m^2, $t_{EC} = 10$ min (synthetic), $t_{EC} = 5$ min (real for Cu and Zn)-20 min (real for Cr), Synthetic: Cr, Cu and Zn = >96, Real: Cr = >91.7, Zn = >95.2, Cu = >94	[10]
Synthetic wastewater (Co = 100 mg/L)	Batch reactor, Al plate electrode, $d = 1$ cm, MP-P	pH$_i$ 8, $j = 62.5$ A/m^2, $t_{EC} = 30$ min, conductivity = 6 mS/cm (NaCl), Co = 99	[11]

(*Continued*)

Table 1 (*Continued*)

Wastewaters containing metal(s)	Types of EC reactor, electrode and connection mode	Optimum operating conditions and removal efficiency (%)	Ref.
Synthetic wastewater (Mn = 100 mg/L)	Batch reactor, Al plate electrode, d = 1 cm, MP-P	pH$_i$ 7, j = 94 A/m^2, t_{EC} = 60 min, conductivity = 7 mS/cm (NaCl), Mn = 94.4	[12]
Synthetic wastewater (Cu = 50 mg/L, Zn = 50 mg/L, Mn = 50 mg/L)	Batch reactor, Al plate electrode, d = 0.5 cm, MP-P	pH$_i$ 7, j = 150 A/m^2, t_{EC} = 5 min (for Cu and Zn), t_{EC} = 35 min (for Mn), Cu and Zn = 100, Mn = 85	[13]
Synthetic wastewater (Cr(III) = 1,700 mg/L, pH 3.4, Cl$^-$ = 1820 mg/L)	Batch reactor, Fe plate electrode, d = 2.2 cm, MP-P and BP-S	j = 335.2 A/m^2, t_{EC} = 50 min, Cr = 99.9 (BP-S), Cr = 81.5 (MP-P)	[14]
Ni-CN electroplating rinse water (Ni = 175 mg/L, Cl$^-$ = 261 mg/L)	Batch reactor, Fe plate electrode, d = 1 cm, MP-P	j = 30 A/m^2, t_{EC} = 80 min, Ni = 99.2, CN$^-$ = 99.7, Operating cost = 2.45 €/m^3	[15]
Cd-CN electroplating rinse water (Cd = 102 mg/L, CN$^-$ = 120 mg/L)	Batch reactor, Fe plate electrode, d = 1 cm, MP-P	j = 60 A/m^2, t_{EC} = 80 min, Cd = 99.4, CN$^-$ = 99.7, Operating cost = 1.05 €/m^3	[15]
Cu production wastewater (Se = 2.32 mg/L, Zn = 85.2 mg/L, Cd = 34.3 mg/L, Cu = 19.5 mg/L, Pb = 5.23 mg/L As = 442 mg/L, pH 4.4)	Continuous reactor, Fe plate, MP-P	j = 48 A/m^2, t_{EC} = 20 min, Q = 3–6 L/h, Se = 98.7, As = 99.9, Cu and Pb = 98.0, Zn and Cd = 99.9	[16]
Synthetic wastewater (Hg = 4.02 mg/L, pH$_i$ 2.7–7.0)	Batch reactor, Fe and Al plate electrode, d = 3 cm, MP-P	j = 80 A/m^2 and t_{EC} = 15 min (for Fe), j = 150 A/m^2 and t_{EC} = 25 min (for Al), Hg = 99.9	[17]
Synthetic wastewater (Cu = 15 mg/L, Cd = 15 mg/L)	Batch reactor, Fe plate electrode, d = 4 cm, MP-P	j = 20.1 A/m^2 (for Cu and pH 7), j = 47.6 A/m^2 (for Cu and pH 12), j = 250 A/m^2 (for Cd and pH 7, j = 927 A/m^2 (for Cd and pH 12), t_{EC} = 45 min, Cu = 96.7 (pH 7), Cu = 98.3 (pH 12), Cd = 49.9 (pH 7), Cd = 96.4 (pH 12)	[18]
Synthetic wastewater (Cr(VI) = 50 mg/L, Cu = 100 mg/L)	Batch reactor, Al electrode, d = 0.5 cm, MP-P	j = 48 A/m^2, C_{NaCl} = 1 g/L and t_{EC} = 50 min (for Cr), j = 48 A/m^2, C_{NaCl} = 5 g/L and t_{EC} = 30 min, Cr(VI) = 85, Cu = 95.1	[19]
Galvanic rinse wastewater (total Cr = 38 mg/L (Cr(VI) = 32.3 mg/L and Cr(III) = 5.70 mg/L), Ni = 3 mg/L, Zn = 8 mg/L)	Batch EC reactor, Fe electrode, d = 1 cm, MP-P, MP-S, BP-S	pH$_i$ 5.4, j = 30 A/m^2, conductivity = 7.98 mS/cm, t_{EC} = 30 min, Cr = 99.77, Ni = 85.62 and Zn = 99.04 (the highest removal efficiency with MP-P), Amount of sludge = 2.32 kg/m^3, Operating cost = 0.70 €/m^3.	This study

Table 2
Characteristics of the galvanic wastewater

Parameters	Value
pH	5.4
Conductivity (mS/cm)	8.0
Cr (total) (mg/L)	38.0
Cr(VI) (mg/L)	32.3
Ni^{2+} (mg/L)	3.0
Zn^{2+} (mg/L)	8.0

were removed by mixing HCl–hexamethylenetetramine aqueous solution [29]. Eight hundred and fifty millilitres of sample wastewater for each experiment was filled in the EC reactor and pH was adjusted to the required pH_i. The electrodes were connected to a digital dc power supply (Agilent 6675A model) and operated at galvanostatic mode. The solution was constantly stirred at 300 rpm with a magnetic stirrer (Heidolp MR 3000D) to reduce the mass transport over potential of the EC reactor. Current and voltage were held constant at desired values for each run and the experiment was started. The samples at the different operating times taken from the EC reactor were filtered using 0.45 µm Millipore membrane and total Cr, Ni and Zn concentrations were analysed. At the end of the run, the electrodes were washed thoroughly with water to remove any solid residues on the surfaces, dried and reweighed. In addition, sludge after the EC experiments was dried at 105°C.

2.3. Analytical procedure

Analyses of the total Cr, Ni and Zn were conducted by the procedures described in the Standard Methods for Examination of Water and Wastewater [28]. The metal concentrations were measured with an ICP Optical Emission Spectrometer (PerkinElmer Optima 7000 DV model). pH and conductivity of GRW before and after the EC process were measured by a pH metre and a conductivity metre (Hach Lange HQ40), respectively. Laboratory-scale experiments were carried out at room temperature. All the chemical reagents used were of analytical grade and all reagents were prepared in Millipore milli-Q deionized water. All the experiments were repeated three times and the average data were reported.

2.4. Operating cost analysis of EC

One of the most important parameters that affected the application of any method of water and wastewater treatment greatly was the operating cost. In this preliminary economic investigation, the cost of the treated GRW (OC, €/m^3) was calculated by considering three parameters as major cost items [30,31], which were amounts of energy and electrode consumptions and chemicals consumed in the process

$$\mathrm{OC} = aC_{\mathrm{energy}} + bC_{\mathrm{electrode}} + cC_{\mathrm{chemicals}} \tag{1}$$

where C_{energy} (kWh/m^3), $C_{\mathrm{electrode}}$ (kg electrode/m^3) and $C_{\mathrm{chemicals}}$ (kg/m^3) are consumption quantities for treated GRW. Unit prices *a*, *b* and *c*, given from the Turkish Market in July 2013, are as follows: *a* is the electrical energy price, at 0.095 €/kWh; *b* is the electrode material price, at 0.85 €/kg for iron; and *c* is the price of H_2SO_4, at 0.29 €/kg, respectively. Costs for C_{energy} and $C_{\mathrm{electrode}}$ calculated from Faraday's law were shown in the following equations:

$$C_{\mathrm{electrode}} = \frac{it_{\mathrm{EC}}M_w}{zFv} \tag{2}$$

$$C_{\mathrm{energy}} = \frac{Uit_{\mathrm{EC}}}{v} \tag{3}$$

where U is cell voltage (V), i is current (A), t_{EC} is the operating time (min) and v is the volume of the treated wastewater (m^3), M_w is the molecular weight of Fe (55.86 g/mol), z is the number of electrons involved in the oxidation/reduction reaction (z = 2) and F is Faraday's constant (96,487 C/mol).

3. Results and discussion

3.1. Effect of electrode connection mode on removal of GRW

Three electrode connection modes (monopolar electrodes in parallel connection (MP-P), monopolar electrodes in serial connection (MP-S) and bipolar electrodes in serial connection (BP-S)) were evaluated for the removal of Cr, Ni and Zn effectively from GRW at pH_i 5.4, 30 A/m^2 and 0–50 min in the EC process using Fe plate electrodes. Batch or continuous mode reactors contained parallel or series plate electrodes with monopolar or bipolar connection [31–34]. Monopolar electrodes required an external electrical contact to the power supply, and their two faces are active with the same polarity. The current was divided between all the electrodes in relation to the resistance of the individual cells at MP-P (Fig. 1(a)). Hence, a lower potential difference was needed in parallel connection when compared with serial connections. MP-S for each pair of sacrificial electrodes was internally connected with each other since the cell voltages sum up, a higher potential difference was required for a given current (Fig. 1(b)). There was no electrical connection between inner electrodes for BP-S. The outer electrodes were only connected to the power supply (Fig. 1(c)). Outer electrodes were monopolar and inner ones are bipolar. The voltage applied between the latter electrodes by the power supply caused the polarization of the intermediate bipolar electrodes. This connection mode has a simple set-up and requires less maintenance cost during the operation.

The removal efficiencies of metal ions from GRW at 10–50 min and pH 5.4 and 30 A/m^2 were varied in the range of 72.88–99.95% for Cr, 40.57–92.01% for Ni and 48.50–99.76% for Zn at MP-P; 62.03–99.53% for Cr, 16.93–85.62% for Ni and 44.19–96.77% for Zn at MP-S; and 46.88–99.01% for Cr, 8.95–82.43% for Ni and 40.48–95.33% for Zn at BP-S connection modes, respectively (Fig. 2). Amounts of sludge and operating costs for the removal of metal ions at three different electrode connection modes were varied as 2.32 kg/m^3 and 0.70 €/m^3 for MP-P, 3.52 kg/m^3 and 0.98 €/m^3 for MP-S and 3.50 kg/m^3 and 1.10 €/m^3 for BP-S, respectively (Table 3). The lowest voltage, energy and electrode consumptions, amount of sludge generated and operation cost were obtained with MP-P electrode connection mode. As a result, MP-P electrode connection mode for the metal ions removal from GRW in the EC process was observed for the most efficient as compared to the rest. The reason behind this was passing of higher current through the electrodes at MP-P connection mode than those for MP-S and BP-S connection modes, which released more Fe^{2+} ions and OH^- ions in the solution leading to the formation of more flocs and thus improved the ability of system to remove metal ions in contrast to other connections [35]. MP-P electrode connection mode was used for the rest of the EC experiments.

3.2. Effect of initial pH on removal of GRW

Initial pH was one of the important factors in affecting the performance of electrochemical process [36]. The variations of metal concentrations with operating time (0–50 min) at different initial pHs (pH$_i$ 2.4–6.4) and MP-P connection mode for Fe electrodes were shown in Table 4. The removal efficiencies of metal ions for Fe electrodes increased with respect to operating time as pH$_i$ was changed from 2.4 to 6.4. The metal concentrations listed in Table 2 decreased from 38.46 to 0.09 mg/L for Cr (98.83%), from 3.13 to 0.45 mg/L for Ni (85.62%) and from 8.35 to 0.08 mg/L for Zn (99.04%), at pH$_i$ 5.4, 30 A/m^2 and 30 min.

The electrolytic dissolution of sacrificial anodes by applying a potential through an external power source undergoes oxidation according to the following equations:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{(reaction at anode)} \tag{4}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad \text{(reaction at anode)} \tag{5}$$

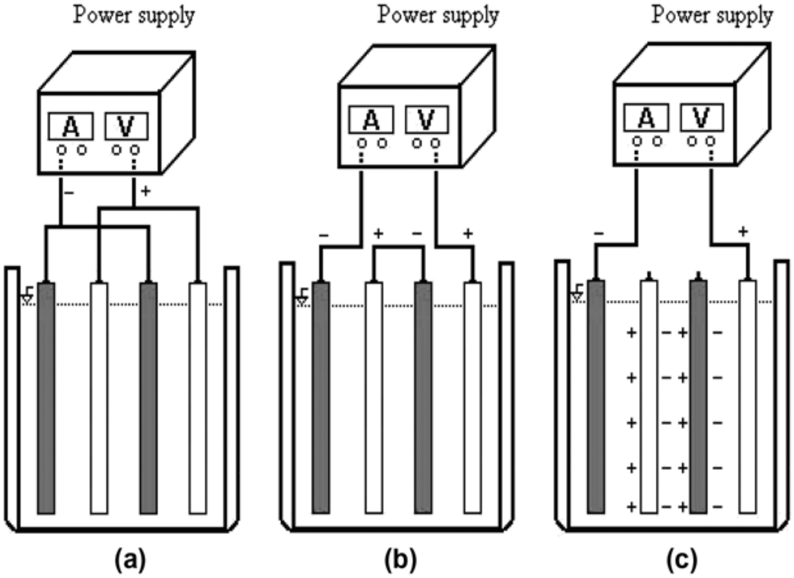

Fig. 1. Three different electrode connection modes used for the treatment of GRW in the EC process: (a) MP-P, (b) MP-S and (c) BP-S.

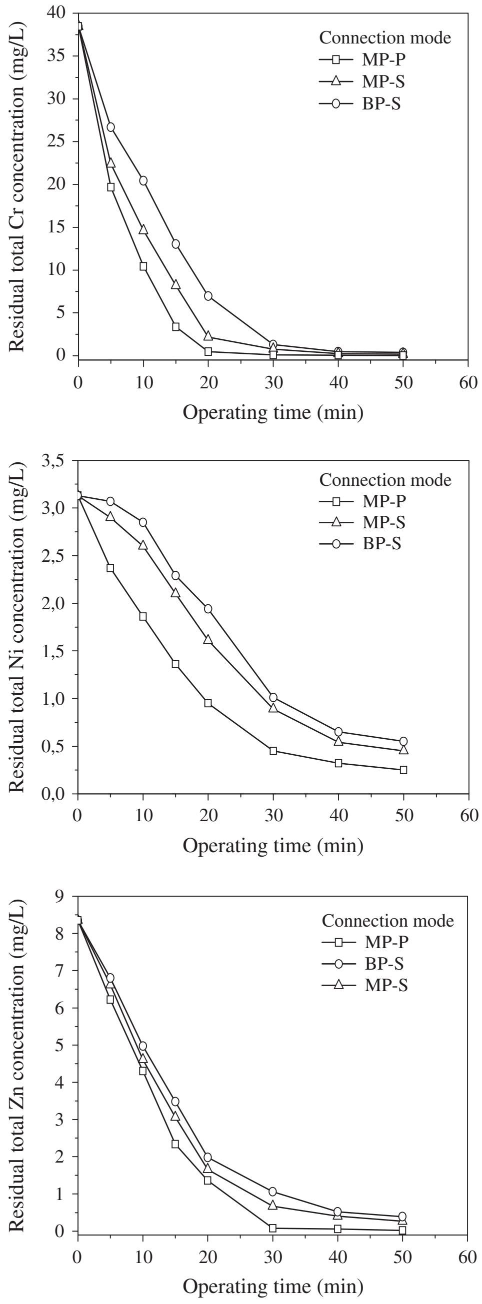

Fig. 2. Effects of electrode connection modes for removals of Cr, Ni and Zn from GRW (pH$_i$ 5.4 and 30 A/m^2).

$$Fe \rightarrow Fe^{3+} + 3e^- \quad \text{(reaction at anode)} \tag{6}$$

The vigorous evolution of H_2 bubbles at the cathode and low evolution of O_2 at the anode are due to the following reactions:

$$2H_2O \rightarrow O_{2(g)} + 4H^+ + 2e^- \quad \text{(reaction at anode)} \tag{7}$$

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \quad \text{(reaction at cathode)} \tag{8}$$

When a direct current is applied between electrodes, Fe^{2+} released by anode oxidation can contribute to coagulant formation. Fe^{2+} can subsequently be oxidized in solution to produce an Fe(III) hydroxide or oxyhydroxide. Coagulants are responsible for aggregation as well as precipitation of suspended particles, and simultaneously, adsorption of dissolved pollutants. Tiny bubbles of hydrogen and oxygen generated at cathode and anode respectively collide with air bubbles and help float the flocculated particles. The hydroxide ions formed at the cathode increase the pH of the wastewater and may induce precipitation of metals in the form of its corresponding hydroxides.

$$Me^{n+}\,(aq) + nOH^- \rightarrow Me(OH)_{n(s)} \tag{9}$$

Ferrous hydroxide particles are produced up to a sufficient concentration to initiate polymerization or condensation reactions illustrated by the following reaction.

$$Fe(OH)_2 + Fe(OH)_2 \rightarrow (OH)Fe - O - Fe(OH) + H_2O \tag{10}$$

The appearance of polymeric complexes [$Fe_2(O)(OH)_2$] allows the removal of metallic pollutants from the wastewater, mainly by adsorption mechanism. The hydroxide polymeric complexes have a considerable sorption capacity [37]. Likewise, the monomer Fe $(OH)_2$ can directly react with metallic pollutants by surface complexation or co-precipitation (as described by Eq. (11))

Table 3
Effect of electrode connection mode on amount of sludge and operating cost

Connection mode	i (A)	U (V)	C_{energy} (kWh/m^3)	$C_{electrode}$ (kg/m^3)	W_{sludge} (kg/m^3)	OC (€/m^3)
MP-P	0.63	1.89	1.20	0.68	2.32	0.70
MP-S	0.63	6.34	3.92	0.71	3.52	0.98
BP-S	0.63	6.75	4.17	0.73	3.50	1.10

Table 4
Effect of pH_i on Cr, Ni and Zn removals from GRW at 30 A/m^2 and MP-P mode

Initial pH	C_{metal} (mg/L)	Operating time (min) 0	5	10	15	20	30	40	50
2.4	Cr	38.46	32.13	24.70	14.05	10.50	3.78	2.05	1.12
	Ni	3.13	2.95	2.43	2.15	1.94	1.67	1.38	1.24
	Zn	8.35	7.75	6.25	5.37	3.53	2.01	1.13	0.90
3.4	Cr	38.46	29.80	20.43	13.03	8.96	2.09	1.06	0.98
	Ni	3.13	2.56	2.11	1.94	1.63	1.16	0.77	0.47
	Zn	8.35	6.89	5.96	4.86	2.60	1.59	0.86	0.65
4.4	Cr	38.46	28.44	16.15	9.93	5.10	0.49	0.40	0.28
	Ni	3.13	2.47	1.97	1.53	1.37	1.05	0.69	0.40
	Zn	8.35	6.38	5.20	3,82	2.05	0.90	0.46	0.32
5.4	Cr	38.46	19.69	10.43	3.37	0.47	0.09	0.06	0.02
	Ni	3.13	2.37	1.86	1.36	0.95	0.45	0.32	0.25
	Zn	8.35	6.22	4.30	2.34	1.36	0.08	0.06	0.02
6.4	Cr	38.46	22.11	14.20	8.90	4.28	0.25	0.08	0.04
	Ni	3.13	2.10	1.46	1.18	0.88	0.65	0.45	0.35
	Zn	8.35	6.20	4.86	2.90	1.66	0.21	0.12	0.08

$$Fe(OH)_2 + Me^{z+} \Leftrightarrow Fe(OH)_{(2-z)}(O)_zMe_{(s)} + zH^+ \tag{11}$$

Eq. (12) also illustrates the surface complexation in which the pollutant can act as a ligand (L) to bind a hydrous iron:

$$L - H_{(aq)} + (HO)OFe_{(s)} \rightarrow L - OFe_{(s)} + H_2O \tag{12}$$

Ferric ions generated by electrochemical oxidation of iron electrode may form monomeric species with respect to pH of the medium, $Fe(OH)_3$ and polymeric hydroxyl complexes, such as $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$, $Fe(OH)_4^-$, $Fe(H_2O)_2^+$, $Fe(H_2O)_5OH^{2+}$, $Fe(H_2O)_4(OH)_2^+$, $Fe(H_2O)_8(OH)_2^{4+}$ and $Fe_2(H_2O)_6(OH)_4^{2+}$. The formation of these hydroxides/polyhydroxides iron compounds have affinity with dispersed particles as well as counter ions. $Fe(OH)_{n(s)}$ remains in the wastewater solution as a gelatinous suspension, which can remove the pollutants from the wastewater by surface complexation or electrostatic attraction followed by co-precipitation and adsorption [12,26,27,32,37].

$Fe(OH)_2$ began to form at approximately pH 5. As a result of using iron electrodes in EC, Fe^{+2} and Fe^{+3} ions were produced by anodic dissolution and $Fe(OH)_2$ and $Fe(OH)_3$ flocs developed in the medium. The decrease in removal efficiency at strong acidic pH was ascribed to an amphoteric behaviour of $Fe(OH)_3$, which led to soluble cations Fe^{3+}, $Fe(OH)^{2+}$ and $Fe(OH)_2^+$ at acidic pH in the literature [4,32]. Moreover, there are several reactions occurring in the bulk solution. Fe^{2+} dissolved at the anode reduces Cr(VI) to Cr(III)

$$Cr_2O_7^{2-} + 6Fe^{2+} + 7H_2O \rightarrow 2Cr^{3+} + 6Fe^{3+} + 14OH^- \tag{13}$$

A slight increase in the pH_i was observed with operating time during the EC process. Values of effluent pH_{final} were changed from 6.23 to 7.26 for Fe

Table 5
Effect of pH_i on amount of sludge generated and operating cost for treatment of GRW

Initial pH	i (A)	U (V)	C_{energy} (kWh/m^3)	$C_{electrode}$ (kg/m^3)	W_{sludge} (kg/m^3)	pH_f (–)	OC (€/m^3)
2.4	0.63	1.86	1.19	0.71	2.18	6.23	0.74
3.4	0.63	1.89	1.20	0.70	2.27	6.46	0.72
4.4	0.63	1.85	1.18	0.69	2.34	6.79	0.71
5.4	0.63	1.89	1.20	0.68	2.32	6.95	0.70
6.4	0.63	1.89	1.21	0.70	2.65	7.26	0.71

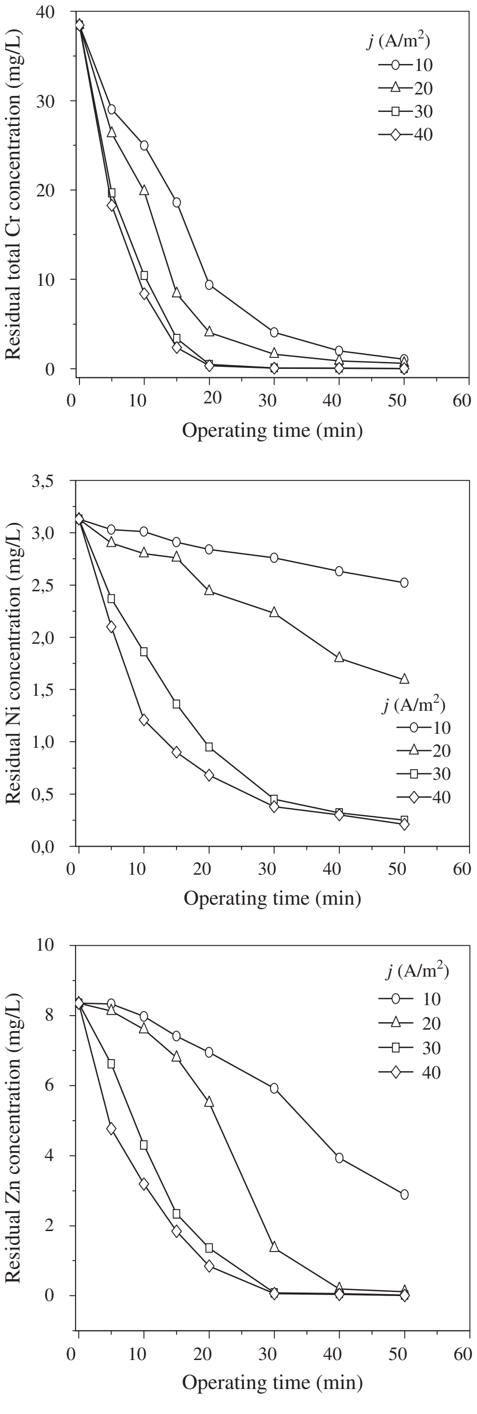

Fig. 3. Effects of current density on Cr, Ni and Zn removals from GRW (pH$_i$ 5.4 and MP-P electrode connection mode).

electrodes when the experiment was operated at pH$_i$ in the range 2.4–6.4 (Table 5). This slight increase of pH value was associated to the formation of hydrogen gas at the cathode and hydroxyl ions (OH^-) produced at the cathode electrode (Eqs. (8), (9) and (13)) in the EC process [29,32,38]. pH$_i$ 5.4 was taken as optimum for all subsequent EC experiments. Amount of sludge and operating cost were varied from 2.18 to 2.65 kg/m^3 and 0.74 to 0.70 €/m^3 at pH$_i$ 2.4–6.4 (Table 5).

3.3. Effect of current density on removal of GRW

Current density is the most important parameter for controlling the reaction rate within the electrochemical reactor in all electrochemical processes [32,39]. It is well known that the current density determines the production rate of coagulant (amount of Fe^{2+} ions released by the anode), also adjusts bubble production, its size and distribution and hence affects the growth of flocs ($Fe(OH)_{2(s)}$ or $Fe(OH)_{3(s)}$ coagulate particles) in the EC reactor [40].

The effect of current density at 10–40 A/m^2, pH$_i$ 5.4 and MP-P electrode connection mode on Cr, Ni and Zn removals from GRW was evaluated. The residual concentrations of Cr, Ni and Zn as a function of the operating time and current density were depicted in Fig. 3. The residual metal concentrations decreased with increasing operating time (0–50 min) from 38.46 to 0.01 mg/L for Cr from 3.13 to 0.21 mg/L for Ni and from 8.35 to 0.01 mg/L for Zn as the current density varied from 10 to 40 A/m^2 (Fig. 3). The results in the figure showed an important drop in the metal ion concentrations along with an increase in the operating time and the current density for Fe electrodes. The efficiency of ion production on the anode and cathode increased since the current density increased. This behaviour was explained at high current densities that the extent of anodic dissolution (Faraday's law, Eq. (2)) increased the metal-hydroxide cationic complexes. Consequently, the removal efficiencies of Cr, Ni and Zn from GRW increased or the residual concentrations of Cr, Ni and Zn in wastewater solution reduced.

Higher dissolution of electrode material (Faraday's law) with high rate of formation of monomeric and/or polymeric iron hydroxides results in significant improvement in metal ions removals from the wastewater mainly due to co-precipitation and adsorption. Indeed, when the wastewater was containing low concentrations of different metals, several reactions occurred: precipitation, co-precipitation and adsorption of metals with ferrous hydroxides. There was probably a good affinity between the metal ions and ferrous hydroxides. It is to be noted that, metals were mainly removed by precipitation, co-precipitation and adsorption using EC [14,29,38,41].

Table 6
Effect of current density on amount of sludge generated and operating cost for treatment of GRW

j (A/m2)	i (A)	U (V)	C_{energy} (kWh/m^3)	$C_{electrode}$ (kg/m^3)	W_{sludge} (kg/m^3)	OC (€/m^3)
10	0.22	1.01	0.22	0.23	1.54	0.22
20	0.43	1.43	0.51	0.45	2.22	0.43
30	0.63	1.89	1.20	0.68	2.32	0.70
40	0.68	1.89	1.25	0.70	2.52	0.72

Values of the operating cost and amounts of sludge produced at 10–40 A/m^2 and pH$_i$ 5.4 were 0.22–0.72 €/m^3 and 1.54–2.52 kg/m^3 (Table 6). The removal of metal ions from GRW in the EC process was found to be very effective in terms of the removal efficiency and operating cost. As seen in Table 1, this study provided as high removal efficiencies as studies in [9,12] except for Ni in terms of operating conditions and metal concentrations present in the wastewater but their studies had four times higher operating cost (97.7 A/m^2 and 45 min) as compared to this study (30 A/m^2 and 30 min). The operating cost was lowered considerably in the EC process.

4. Conclusions

The present study dealt with the removal of heavy metal ions from GRW by the EC method using iron plate electrodes with three electrode connection configurations. The results indicated that the EC with Fe electrodes at MP-P connection mode was very efficient and was able to achieve 99.77% Cr, 85.62% Ni and 99.04% Zn removal at an EC time of 30 min, a current density of 30 A/m^2 and pH 5.4 with operating cost of 0.70 €/m^3, respectively. The EC process showed a great potential in the heavy metals removal from GRW. Cr, Ni and Zn removal efficiency increased with increasing current density. At higher current density, the formation rate of iron hydroxide flocs increased. The removal mechanism of metal ions from the wastewater in the EC process might be co-precipitation and adsorption with metal hydroxides. The final effluent pH at the optimum operating conditions in the EC process was 6.95, which fell into the limit range values set by Turkish Water Pollution Control Regulation. The results demonstrated the technical feasibility of the EC process as a reliable method for removal of heavy metals from industrial wastewaters. The EC process has the potential for cost-effective removal of heavy metals from water and wastewaters.

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