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Optimization of electrocoagulation (EC) process for the purification of a real industrial wastewater from toxic metals

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ABSTRACT

In the present work, the efficiency evaluation of electrocoagulation (EC) in removing toxic metals from a real industrial wastewater, collected from Aspropyrgos, Athens, Greece was investigated. Manganese (Mn), copper (Cu) and zinc (Zn) at respective concentrations of 5 mg/L, 5 mg/L and 10 mg/L were present in the wastewater (pH = 6), originated from the wastes produced by EBO-PYRKAL munitions industry and Hellenic Petroleum Elefsis Refineries. The effect of operational parameters such as electrode combination and distance, applied current, initial pH and initial metal concentration, was studied. The results indicated that Cu and Zn were totally removed in all experiments, while Mn exhibited equally high removal percentages (approximately 90%). Decreasing the initial pH and increasing the distance between electrodes, resulted in a negative effect on the efficiency and energy consumption of the process. On the other hand, increasing the applied current, favored metal removal but resulted in a power consumption increase. Different initial concentrations did not affect metal removal efficiency. The optimal results, regarding both cost and EC efficiency, were obtained with a combination of iron electrodes, at 2 cm distance, at initial current of 0.1 A and pH = 6. After 90 min of treatment, maximum removal percentages obtained were 89% for Mn, 100% for Cu and 100% for Zn, at an energy consumption of 2.55 kWh/m^3.

1. Introduction

Toxic metals comprise a group of minerals that have no known function in the human body and are, in fact, harmful. Their presence in industrial wastewaters is one of the major environmental pollution issues. Industrial wastewaters, containing toxic metals, are discharged increasingly into the environment, mainly due to the rapid development of industries involving mining, electroplating or smelting operations which contain various kinds of toxic substances (Al Aji et al., 2012). The majority of metals (e.g. Mn, Zn and Cu) are considered harmful when being discharged without treatment, mostly due to their non-biodegradability, toxicity and/or carcinogenicity (Adhoum et al., 2004; Hunsom et al., 2005; Heidmann and Calmano, 2008a; Hahladakis et al., 2013). Various techniques have been implemented for the pollution abatement of wastewaters from toxic metals which include adsorption (Chen and Wang, 2000), chemical precipitation (Matlock et al., 2002; Meunier et al., 2006), ion-exchange (Sapari et al., 1996), biosorption (Chen et al., 2008; Witek-Krowiak et al., 2011), membrane filtration (Blöcher et al., 2003; Song et al., 2011), coagulation–flocculation (Hankins et al., 2006; Heredia and Martín, 2009; Vedrenne et al., 2012), flotation (Blöcher et al., 2003; Polat and Erdogan, 2007; Sudilovskiy et al., 2008) and electrocoagulation (EC) (Mouedhen et al., 2008; Heidmann and Calmano, 2008a, 2008b; Merzouk et al., 2009; Kabdaşlı et al., 2009; Pociecha and Lestan, 2010; Heidmann and Calmano, 2010; Shafaei et al., 2011; Hanay and Hasar, 2011; Al Aji et al., 2012).

EC is a water treatment process which involves the application of electric current across metal electrodes to remove various contaminants. It is a reliable method, coupled with environmental and economic benefits (Trompette and Vergnes, 2009), which has been applied sufficiently for the removal of various pollutants from wastewater effluents containing toxic metals (Merzouk et al., 2009; Shafaei et al., 2011), oil wastes (Tir and Moulai-Mostefa, 2008; Maha Lakshmi and Sivashanmugam, 2013), arsenic (Gomes et al., 2007; Wan et al., 2011) and COD (Zongo et al., 2009; Wang et al., 2009). Furthermore, EC has been reported to successfully treat drinking water (Ghosh et al., 2008; Malakootian et al., 2010), galvanic (Heidmann and Calmano, 2010) and/or metal plating wastewater (Kabdaşlı et al., 2009; Akbal and Camci, 2011).

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According to Mollah et al. (2001) advantages of EC include: the requirement of a simple and easy operational equipment which transforms the treated wastewater to a clear, odorless and colorless effluent, producing, at the same time, low amount of sludge. In addition, there are some differences between flocs produced in an EC process and chemical flocs. The first ones can be separated faster by filtration than the latter and on top of that, they are more stable and contain less bound water (Mouedhen et al., 2008).

In the present study an EC reactor was designed for the removal of Mn, Cu and Zn from a real industrial wastewater originated, mainly, from oil refineries situated in Aspropyrgos, Athens, Greece. Further details associated with the real wastewater used in the experiments are presented in Section 2.1. To the authors best knowledge, few works have been published in the treatment of real industrial effluents via EC (Shafaei et al., 2011), hence the significance and innovation of the present work. It is more common, instead, the study of synthetic (Hanay and Hasar, 2011), galvanic (Heidmann and Calmano, 2010) and model (Vlachou et al., 2013) wastewaters with high initial metal concentrations. Furthermore, there are few studies that have dealt with the removal of Mn (Hanay and Hasar, 2011; Shafaei et al., 2011; Al Aji et al., 2012) and possibly none with the combination of Mn, Cu and Zn, present in relatively low initial concentrations (approximately 5 mg/L, 5 mg/L, and 10 mg/L, for the respective elements), as it usually happens in real wastewaters. In addition, the effect of operational parameters, such as material and distance of electrodes, applied current, initial pH and initial metal concentrations, was investigated. Finally, removal rates, maximum metal removal percentages, sacrificial anode mass loss and power consumption were calculated in each experiment and the optimal operating conditions-regarding cost and efficiency-were determined.

2. Materials and methods

2.1. Real industrial wastewater characteristics

The real wastewater was collected from the industrial zone of Aspropyrgos, Athens, Greece. Hellenic Defense Systems S.A. (EBO-PYRKAL) and Hellenic Petroleum Elefsis Refineries are the main industries present at the surrounding area, producing wastes. At the collection spot (through a naturally shaped type of a well), a mixture of wastewater and seawater was sampled, hence the elevated initial electrical conductivity of the wastewater used in the experiments (~7 mS/cm). The real wastewater was acidified (290 μL HNO_3 Fluka, Nitric acid Salpetersäure, per 10 mL of sample) directly after sampling for preventing any metal precipitation. The initial pH value was approximately 6. Ten metals were originally chosen to be measured (some not even detected, hence not reporting them) in the real wastewater but three of them were selected (with regard to their total concentration) for studying their removal via EC. In general, the higher the initial metal content, the better removal percentages can be obtained and the EC process is facilitated. These metals were Mn, Cu and Zn at concentrations of approximately 5 mg/L, 5 mg/L and 10 mg/L, respectively.

2.2. Batch experiments

Experiments were conducted by the use of a 500 mL beaker, placed on a magnetic stirrer at 150–200 rpm. The pair of iron and/or aluminum electrodes (Erlikon SA – Sidenor, General purpose electrode Fincord-M) were cylindrical (Ø = 3.25 mm) and were installed vertically in the beaker. The active electrodes surface was 7.14 cm^2 and the initial distance between them was 2 cm. A constant current was provided by a DC power supply (Statron, 0–1.2 A, 0–300 V). The experimental set up is shown in Fig. 1. Samples were periodically taken every 10 min, filtered (0.45 μm) and acidified (290 μL HNO_3 Fluka, Nitric acid Salpetersäure, per 10 mL of sample) for further determination of the selected-examined toxic metal concentrations by the use of an ICP-MS (Agilent 7500-CX). The total duration time of the experimental process was 90 min.

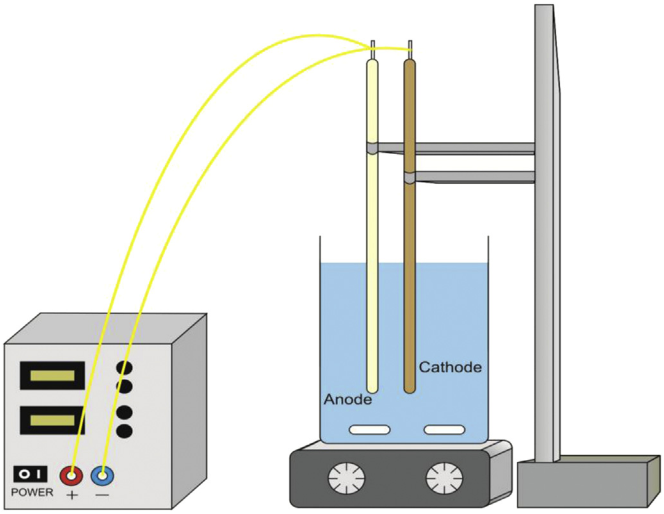

Fig. 1. The experimental EC set up.

Only to further investigate the effect of initial metal concentrations, stock solutions of 1000 mg/L Mn, Cu and Zn were prepared by using $Mn(NO_3)_2$, $CuSO_4 \cdot 5H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$, respectively. The examined spiked wastewater had, then, initial concentrations of 10 mg/L and 20 mg/L, regarding Mn and Cu and 20 mg/L and 40 mg/L, regarding Zn. The experiments were, in turn, conducted with initial pH values that varied between 2 and 6, adding HNO_3 to adjust the pH; thus, the effect of different initial pH was, also, examined.

In the real wastewater, the presence of TPHs and PAHs was detected, first by smell and measured, in turn, but the reporting of their concentration values or of the implications they have, possibly, created in the overall efficiency of the EC process (Adhoum et al., 2004; Baker and Head-Gordon, 2010) was considered beyond the aim and scope of the present study. This experimental perspective could, as well be, the theme of a future research in the pollution abatement of real wastewaters via EC.

2.3. Measurements

At the beginning of each experiment (t = 0), initial conductivity and pH were measured with a Crison CM 35 Conductivity-meter and a Crison pH-meter GLP21, respectively. The initial concentrations of the selected toxic metals (Mn, Cu and Zn) were, also, determined by an ICP-MS, as mentioned above. During the 10 min sampling process, between intervals and till the end of each experiment, pH, electrical conductivity and residual metal concentrations of each liquid sample were measured. Finally, the anode electrode mass loss was calculated as described in the following Section 2.4.

2.4. Calculations

Both at the beginning (t = 0) and at the end (t = 90) of each experiment, the dissolution rate of the anode was calculated by the difference in the weight of the electrode, after rinsing and drying it, successively.

According to Faraday's law, the theoretical maximum dissolved mass of iron or aluminum, from the sacrificial anode in a specific electrical current during EC process, is calculated by the mathematical expression (Mollah et al., 2004):

$$m = \frac{I \cdot t \cdot M_r}{z \cdot F} \tag{1}$$

where *m* is the amount of the dissolved anode material (g), *I* the applied current (A), *t* the electrolysis time (s), M_r the specific molecular weight of the anode (aluminum or iron) (g/mol), *z* the number of electrons involved in the reaction and *F* the Faraday's constant (96,485.34 As/mol).

The total amount of toxic metals removal was calculated from the difference between the initial and the final concentration of each metal in each experiment, whereas removal percentages were obtained via the following formula:

$$\text{Removal efficiency} = \frac{C_o - C_i}{C_o} * 100\% \tag{2}$$

where C_i is the concentration of the each examined metal at time t and C_o is the initial concentration of the metal.

The linear gradient between metal removal (μmol/L) and charge loading (As/L) was used for calculating the removal rates of the removed metal, in μmol per inserted charge loading (μmol/As).

The energy consumption *E* (kWh/m^3) of the overall EC treatment of the real industrial wastewater was calculated with the following equation:

$$E = \frac{U \cdot t \cdot I}{V} \tag{3}$$

where *U* is the required voltage (V), *t* the required EC time (h), *I* the applied current (A), and *V* the volume (m^3).

All the main mechanisms and physicochemical reactions involved in EC process, along with the formation of a variety of coagulant species and metal hydroxides, which accumulate, destabilize and adsorb the dissolved contaminants have been reported in detail in various studies and therefore will not be repeated in the present one (Mollah et al., 2001, 2004; Heidmann and Calmano, 2010; Vlachou et al., 2013).

3. Results and discussion

3.1. Effect of combination of electrodes

In the EC process, the combination of electrodes is an important factor which affects the toxic metal removal efficacy. In the present work, four electrode combinations were tested to determine the optimal; Fe–Fe, Fe–Al, Al–Fe and Al–Al. The other parameters of the real wastewater involved initial metal concentrations (5 mg/L Mn, 5 mg/L Cu and 10 mg/L Zn), at pH = 6 and an applied current of 0.5 A. The initial distance of electrodes was 2 cm and the results obtained are presented in Table 1. The removal percentages of all three metals were sufficiently high, 95–99% for Mn, 100% for Cu and 100% for Zn, for all tested combinations. Furthermore, when using Fe–Fe electrodes, the residual concentrations were 0.21 mg/L for Mn and 0 mg/L for Cu and Zn, with respective removal percentages of 95%, 100% and 100%. As it can be inferred from Table 1, similar behavior was observed when the other three combinations of electrodes were examined; with Fe–Al, Al–Fe and Al–Al the total Mn removal percentages obtained were 96%, 98% and 99%, respectively. Cu and Zn were completely removed in all the aforementioned cases.

After 90 min of treatment, the highest metal removal was achieved with the Al–Al electrode combination. As the results indicated, metal removal efficiencies were slightly higher using aluminum at the anode, even though all three toxic metals exhibited almost zero residual concentrations for all tested electrode combinations. Using iron at the anode, though, increases the energy consumption and the final pH of the wastewater, than using aluminum.

Table 1
Residual metal concentrations (mg/L), metal removal (%), removal rates (μmol/A s) of Mn, Cu and Zn, anode mass loss, final pH and energy consumption for different electrode combinations after 90 min of EC treatment with initial concentrations of 5 mg/L Mn, 5 mg/L Cu and 10 mg/L Zn and initial pH 6.

	Fe–Fe	Fe–Al	Al–Fe	Al–Al
Residual metal concentration (mg/L)				
Mn	0.21 ± 0.007	0.17 ± 0.0002	0.06 ± 0.001	0.03 ± 0.0006
Cu	0	0	0	0
Zn	0	0	0	0
Removal (%)				
Mn	95	96	98	99
Cu	100	100	100	100
Zn	100	100	100	100
Removal rate (μmol A^{-1} s^{-1})				
Mn	7.63	8.50	10.63	9.63
Cu	4.15	6.51	4.20	4.49
Zn	9.29	7.74	7.80	12.63
Anode mass loss (g)	0.93	0.66	1.94	1.91
End pH	9.26	7.67	6.24	6.26
Energy consumption (kWh/m^3)	98.25	60.75	15.0	12.75

The main objective of these experiments was to determine the difference between Fe and Al used at the anode. It is also noteworthy, that Al is much more expensive than Fe (about thrice the price of the latter), not to mention that Al electrodes are consumed much faster than Fe electrodes. These were, practically, the main reasons for choosing to use Fe at the cathode in all the rest of the experiments, despite being more energy consuming. Consequently, the effect of the other parameters involved in the EC process and which are reported in the following Sections (3.2–3.6), are examined in experiments that employ only Fe–Fe and Al–Fe as electrode combinations and, in some cases, only Fe–Fe.

3.2. Effect of applied current

The effect of the applied current on removal of metals from the real industrial wastewater was studied. The experiments were conducted with initial pH = 6, using Fe–Fe and the Al–Fe electrodes and applied currents of 0.5, 0.3 and 0.1 A. The distance between electrodes was kept at 2 cm. The profile of each metal concentration is presented in Fig. 2, while Table 2 presents all the detailed calculations regarding removal rates, anode mass loss, energy consumptions and maximum removal percentages of metals for all applied currents. As it is shown from Fig. 2, by increasing electric current, the removal process is accelerated and the residual metal concentrations are quickly decreased. This observation has also been reported in various other studies (Heidmann and Calmano, 2008a, 2010; Shafaei et al., 2010; Shafaei et al., 2011; Al Aji et al., 2012). According to Faraday's law (Eq. (1)), higher applied currents lead to greater production of ions, thereby enhancing the EC process. Regarding Mn removal, Fe–Fe electrodes and Al–Fe electrodes demonstrated equally high removal percentages (>95%) at 0.5 A. When the Fe–Fe electrode combination was used, increasing the current from 0.1 to 0.5 A did not much affect maximum removal percentages (89%–95%). On the other hand, the Mn removal in the Al–Fe electrode system was accelerated and the residual concentrations decreased significantly when the current increased from 0.1 to 0.5 A. More information regarding

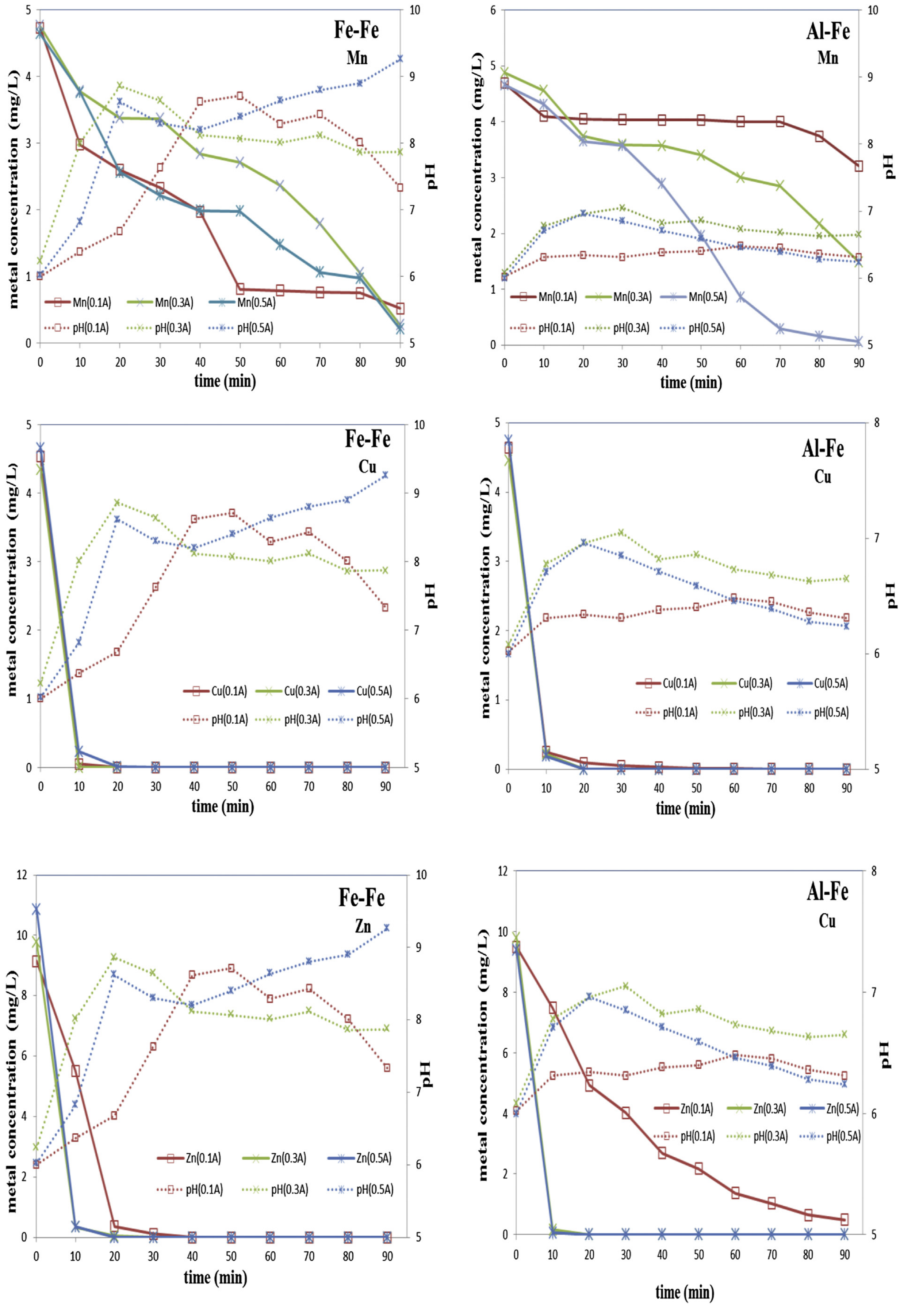

Fig. 2. Profile of Mn, Cu and Zn metal concentrations and of pH of the real industrial wastewater during EC, using Fe–Fe and Al–Fe electrodes at applied currents of 0.5, 0.3 and 0.1 A.

Table 2
Residual metal concentrations (mg/L), metal removal (%), removal rates (μmol/A s) of Mn, Cu and Zn, anode mass loss, final pH and energy consumption for different applied currents after 90 min of EC process with initial concentrations of 5 mg/L Mn, 5 mg/L Cu and 10 mg/L Zn and initial pH 6, using a Fe–Fe and an Al–Fe electrode system.

	Fe–Fe			Al–Fe		
Applied current (A)	0.5	0.3	0.1	0.5	0.3	0.1
Residual metal concentration (mg/L)						
Mn	0.21 ± 0.007	0.27 ± 0.008	0.52 ± 0.008	0.06 ± 0.001	1.49 ± 0.05	3.21 ± 0.03
Cu	0	0	0	0	0	0
Zn	0	0	0	0	0	0.49 ± 0.002
Removal (%)						
Mn	95	94	89	98	69	31
Cu	100	100	100	100	100	100
Zn	100	100	100	100	100	95
Removal rate (μmol A^{-1} s^{-1})						
Mn	7.63	7.79	7.55	10.63	5.92	1.79
Cu	4.15	3.73	3.92	4.20	3.95	4.2
Zn	9.29	8.39	11.41	7.80	8.26	14.53
Anode mass loss (g)	0.93	0.86	0.5	1.94	1.53	1.62
End pH	9.26	7.87	7.33	6.24	6.65	6.31
Energy consumption (kWh/m^3)	98.25	25.2	2.55	15.0	5.4	0.9

the removal behavior of Mn with Al–Fe electrodes is provided by the removal rates presented in Table 2, where the highest rate was obtained at 0.5 A. Under the highest examined current of 0.5 A, maximum Mn removal percentage obtained was 95% with Fe–Fe electrodes system and 98% with Al–Fe combination, leaving a residual concentration of <0.2 mg/L. On the other hand, Cu and Zn maximum removal reached 100% both with Fe–Fe and Al–Fe electrode systems, for all three current intensities (0.1, 0.3 and 0.5 A). Energy consumption exhibited its highest value at the highest current used (0.5 A) for both electrode systems, Fe–Fe and Al–Fe (see Table 2).

Fig. 3 presents the theoretical and experimental anode electrode mass loss during the 90 min EC treatment of the real wastewater under different applied currents. According to Faraday's law (Eq. (1)), the relationship between anode mass loss and applied current is expected to be linear. This behavior is observed in the graphs of Fig. 3. Experimental mass loss was higher than the theoretical for both electrode materials used for anode (Fe or Al). Furthermore, aluminum mass loss measured in absolute values was higher than that corresponded to iron. In all experiments, pH of the medium was raised during EC process.

The subsequent experimental investigation proceeded choosing 0.3 A as the preferred applied current. At 0.1 A, the removal percentage of Mn was only 31% for an Al–Fe combination, whereas at 0.5 A the energy consumption remained at high levels, in comparison with 0.1 and 0.3 A. Thus, the applied current of 0.3 A was selected, which led to low Mn residual concentrations and to a complete removal of Cu and Zn.

3.3. Effect of distance between electrodes

The effect of distance between electrodes in the removal of the selected metals from the real wastewater was examined under a constant current of 0.3 A, with Fe–Fe and Al–Fe electrodes system. As illustrated in Fig. 4, increasing the distance between Fe electrodes from 2 to 4 cm affects negatively the removal percentage of Mn, whereas regarding the Al–Fe electrode combination, a slight increase of the total removal percentage of Mn was observed. Cu and Zn were removed completely but at a slower rate when the distance increased. Further details regarding the efficiency of the EC, the energy consumption and the removal rates can be seen in Table 3. Concluding, concerning the overall efficiency of the EC procedure, the best results were observed for the smallest tested distance of 2 cm.

3.4. Effect of initial pH

The initial pH of the solution is considered to be one of the most important factors affecting, considerably, the overall EC process (Arroyo et al., 2009; Chen, 2004). The effect of the initial pH on metal removal from the real wastewater was studied on a range of approximately 2–6, for Fe–Fe and Al–Fe electrode combinations,

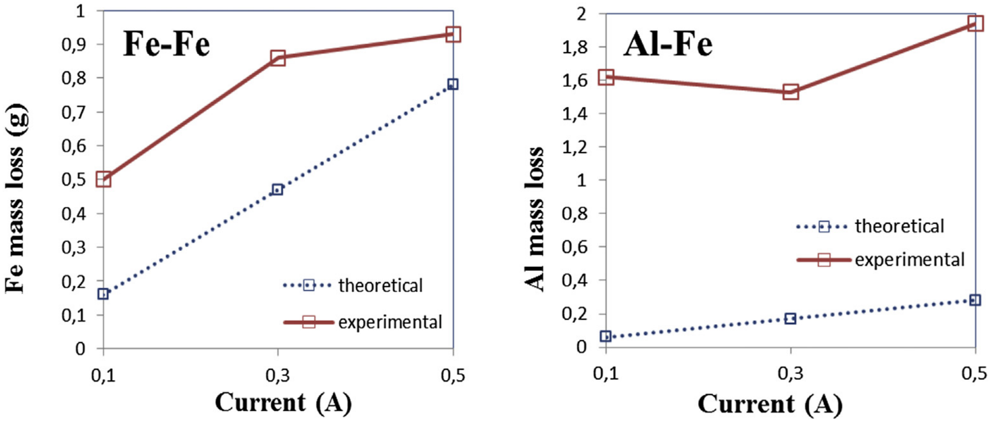

Fig. 3. Effect of applied current on the experimental anode mass loss, in comparison with the theoretically expected.

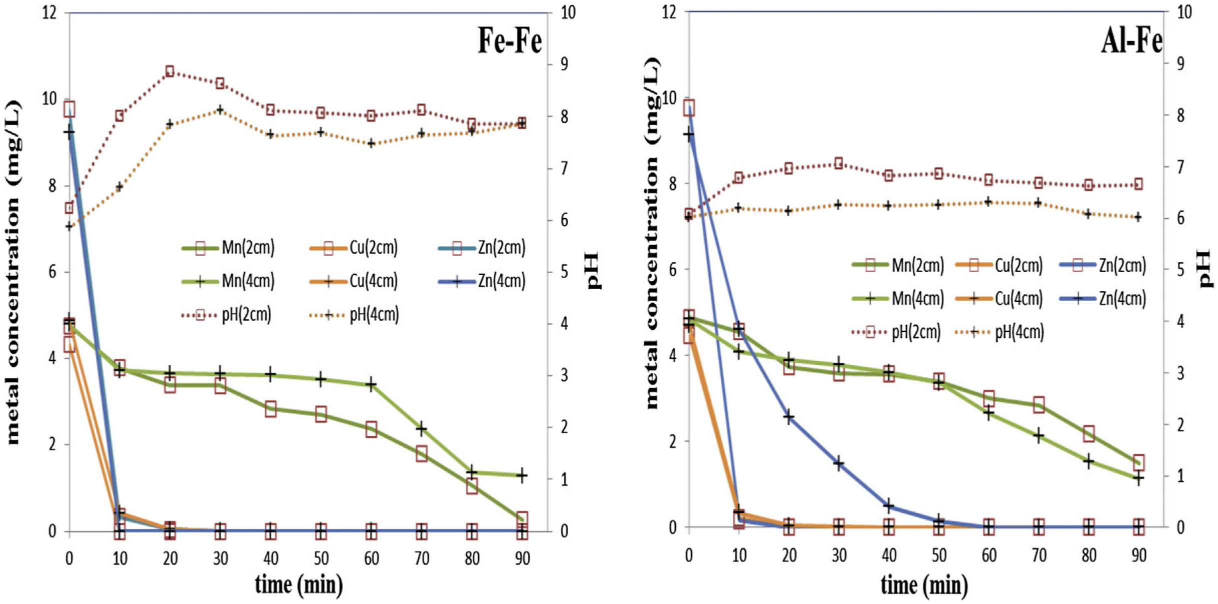

Fig. 4. Effect of distance between electrodes on metal concentration profile, using Fe–Fe and Al–Fe electrode system at an applied current of 0.3 A.

at a steady electric current of 0.3 A and 90 min of EC treatment.

In general, the pH of the medium raises during EC as a result of the electrochemical process and the production of hydroxyl ions in the aqueous solution. According to the results, by using a Fe–Fe electrode system, the decrease in the initial pH did not favor the EC efficiency (e.g. lower Mn removal percentages), whereas no substantial difference in the metal removal occurred, when Al was used at the anode (see Table 4). With iron electrodes used at the initial wastewater (pH = 6), the Mn removal reached almost 94%, with a final pH value of 7.87, after 90 min of EC treatment and an anode mass loss of 79%, that was greater than the theoretically expected. On the other hand, using the Al–Fe combination at the same initial pH, Mn removal percentage obtained was merely 69%, with a final pH value of 6.65, after 90 min of EC treatment and an anode mass loss much lower than the theoretically expected. At initial pH = 4, the maximum Mn removal achieved was 62% for a Fe–Fe system and 70% for an Al–Fe system, while final pH was 7.4 and 6.5, respectively.

By decreasing pH, residual metal concentrations are expected to increase. Low pH does not favor hydroxides and hydroxyl ions formation and consequently inhibits the EC procedure, a conclusion also reported by Heidmann and Calmano (2010).

In continuing the pH effect experiments, a further decrease of the initial pH to approximately 2, limited the Mn removal percentage only to 56%, when using Fe–Fe electrodes, whereas with the Al–Fe system a mere 67% removal was measured, sustaining the above mentioned conclusion. Nevertheless, the decrease of the initial pH did not have any effect to the final removal percentages of Cu and Zn. Comparing the two examined electrode combinations, it can be inferred that when using Fe–Fe electrodes and decreasing the initial pH, the EC procedure is not favored, as regards the Mn removal, whereas its efficacy in removing Mn was kept in the same order of magnitude for all three tested initial pH, when an Al–Fe system was used. Concluding, a pH value around 6 (which was the approximate initial value of the real industrial wastewater) is considered to be the optimal, especially when an iron electrode is used at the anode.

Table 3
Residual metal concentrations (mg/L), metal removal (%), removal rates (μmol/A s) of Mn, Cu and Zn, anode mass loss, final pH and energy consumption for different electrode distance after 90 min of EC treatment with initial concentrations of 5 mg/L Mn, 5 mg/L Cu and 10 mg/L Zn and initial pH 6, using a Fe–Fe and an Al–Fe electrode system at 0.3 A.

	Fe–Fe		Al–Fe	
Electrode distance (cm)	2	4	2	4
Residual metal concentration (mg/L)				
Mn	0.27 ± 0.008	1.28 ± 0.03	1.49 ± 0.05	1.13 ± 0.02
Cu	0	0	0	0
Zn	0	0	0	0
Removal (%)				
Mn	94	73	69	76
Cu	100	100	100	100
Zn	100	100	100	100
Removal rate (μmol A^{-1} s^{-1})				
Mn	7.79	6.12	5.92	7.05
Cu	3.73	4.49	3.95	4.30
Zn	8.39	7.71	8.26	12.24
Anode mass loss (g)	0.86	0.68	1.53	1.91
End pH	7.87	7.86	6.65	6.02
Energy consumption (kWh/m^3)	25.2	27	5.4	5.85

3.5. Effect of initial metal concentrations

The effect of the initial metal concentration on their removal was studied with Fe–Fe and Al–Fe electrode systems, at a 2 cm electrode distance and at an initial current of 0.3 A, for a 90 min EC treatment. In doing so, the real wastewater was spiked with Mn, Cu and Zn, as described in Section 2.2. The examined concentrations for both Mn and Cu were approximately 5 mg/L (initial), 10 mg/L and 20 mg/L (spiked) and for Zn 10 mg/L (initial), 20 mg/L and 40 mg/L (spiked), hence twice and four times the initial metal concentrations of the real industrial wastewater (see Fig. 6). As illustrated in Fig. 5, when increasing the initial concentration of Mn, its total removal percentage is still maintained in the same order of magnitude (>90%) for a Fe–Fe electrode combination, whereas using an Al–Fe system, the Mn total removal percentage is enhanced. A further increase in the Mn initial concentrations causes its removal to be quicker in the first minutes of treatment, in

Table 4
Residual metal concentrations (mg/L), metal removal (%), removal rates (μmol/A s) of Mn, Cu and Zn, anode mass loss, energy consumption and final pH for different initial pH after 90 min of EC treatment, with initial concentrations of 5 mg/L Mn, 5 mg/L Cu and 10 mg/L Zn.

	Fe–Fe			Al–Fe		
Initial pH	6	4	2	6	4	2
Residual metal concentration (mg/L)						
Mn	0.27 ± 0.008	1.81 ± 0.02	2.03 ± 0.03	1.49 ± 0.05	1.39 ± 0.06	1.61 ± 0.05
Cu	0	0	0	0	0	0
Zn	0	0	0	0	0	0
Removal (%)						
Mn	94	62	56	69	70	67
Cu	100	100	100	100	100	100
Zn	100	100	100	100	100	100
Removal rate (μmol A^{-1} s^{-1})						
Mn	7.79	5.37	4.35	5.92	7.14	8.32
Cu	3.73	5.06	7.12	3.98	4.99	4.70
Zn	8.39	9.8	13.93	8.26	12.38	14.28
Anode mass loss (g)	0.86	0.77	0.61	1.53	1.76	1.78
End pH	7.87	7.4	7.92	6.65	6.5	6.38
Energy consumption (kWh/m^3)	25.2	15.3	18	5.4	5.85	6.3

contrast to Zn (see Fig. 6). In addition, Mn maximum removal percentages were obtained when the highest initial concentration (20 mg/L) was used with a Fe–Fe pair of electrodes. On the other hand, the removal of Cu was found independent from initial metal concentrations, for both Fe–Fe and Al–Fe systems, exhibiting total removal in all cases (100%). Regarding Zn, the maximum removal percentage was 100%, meaning that it was also independent to the initial metal concentrations, for both electrode combinations, an observation also reported by Heidmann and Calmano (2008b).

Removal efficacy of Mn increased from 94% to 97% (using Fe–Fe electrodes) and from 69% to 94% (using Al–Fe electrodes) when initial concentration increased from 5 to 20 mg/L, with conductivities ranging from approximately 4 to 5 mS/cm, during a 90 min EC treatment. The removal efficacies of Cu and Zn were not affected by the initial metal concentrations or the electrode combinations (100% removal), while conductivities ranged from 4 to 5 mS/cm. The removal rates, though, were changed rapidly, especially at the beginning of the EC process for all three tested metals, when using Fe–Fe electrodes (up to 10 min for Mn, Cu and Zn) while afterwards the slope of the curve dropped off (see Fig. 6).

Table 5 sums up the calculations and the results for the removal of all three metals. Regarding the removal rates, values get higher with increasing the metal concentrations, in all experiments for all tested cases and combinations. This trend could, possibly, be related to the fact that the higher the content of metals in the solution is, the faster the reactions at the electrodes occur. Removal percentages may still be in the same order of magnitude, but by increasing the initial metal concentration, the total amount of removed toxic metals becomes greater.

During the EC process, coagulants are produced through the formation of hydroxides, while the pH of the solution increases with elapsed time (see Fig. 6). Initial pH for all tested samples was approximately between 5 and 6, and final pH values ranged from 6.5 to 8.5. As the concentrations of toxic metals decrease, during EC process, pH value increases due to the hydroxide ions formed at the cathode.

In all experiments, the removal rate of Mn is slower than that of Cu and Zn. As it is also reported by Shafaei et al. (2011), the differences in the removal rates between Mn, Cu and Zn may be attributed to the difference in the solubility of these metals in the wastewater. The co-precipitation of all the metallic hydroxides, thus $Mn(OH)_2$, $Cu(OH)_2$ and $Zn(OH)_2$ could have played a dominant role in the removal mechanism of metals (Adhoum et al., 2004; Shafaei et al., 2010). It should also be taken into consideration that the solubility constants (Ksp) of Mn, Cu and Zn hydroxides at 25 °C are 1.9×10^{-13}, 2.2×10^{-20} and 1.2×10^{-17}, respectively. Thus, it can be inferred that under the same conditions, Mn ions would be removed slower than Cu and Zn ions (Shafaei et al., 2011).

3.6. Energy consumption profile

Energy consumption was calculated according to the mathematical expression (3), reported in Section 2.4. It is directly proportional to the electrical current and voltage used and, consequently, experiments that were performed under higher currents required higher energy. As the results in Tables 1–5 indicate, energy consumption differed when using Fe–Fe and Al–Fe electrodes. More specifically, the use of iron at the anode was found to be more energy consuming than using aluminum (see Table 1). Furthermore, a general observation that can be inferred is that higher applied currents led to higher energy expenditure (see Table 2). Regarding the effect of distance between electrodes, of initial pH and of initial metal concentrations on energy consumption, it was observed that energy expenditure was kept in the same order of magnitude for all EC experiments (see Tables 3–5).

It should also be noticed that even though iron is more energy consuming than aluminum, it is about three times cheaper, thus it is preferred as an anode electrode (see Table 1). Best results regarding removal of toxic metals and energy consumption were obtained with a combination of iron electrodes, placed at a 2 cm distance, at a current of 0.1 A and at initial pH = 6. After 90 min of treatment, total removal percentages reached almost 100%, at an energy consumption of 2.55 kWh/m^3. The total cost of this option per m^3, which contains the energy consumed per m^3 of treated wastewater and the cost of the electrode mass loss, is 1.32 €/m^3 (the current average electrical energy price in Greece is 0.10 €/kWh).

3.7. Comparison with literature data

Table 6 sums up the results of other related works for the removal of toxic metals from wastewaters via EC process. The results include values only for the metals which were studied in the present research. It is noteworthy that initial metal concentrations reported in other studies are relatively high and that is mainly due to the nature of the wastewater used (model wastewater). To the authors best knowledge, the majority of literature data reports studies that have dealt with synthetic, galvanic and model wastewaters, usually spiked with such high initial metal concentrations.

Similarities of other studies compared to the present research

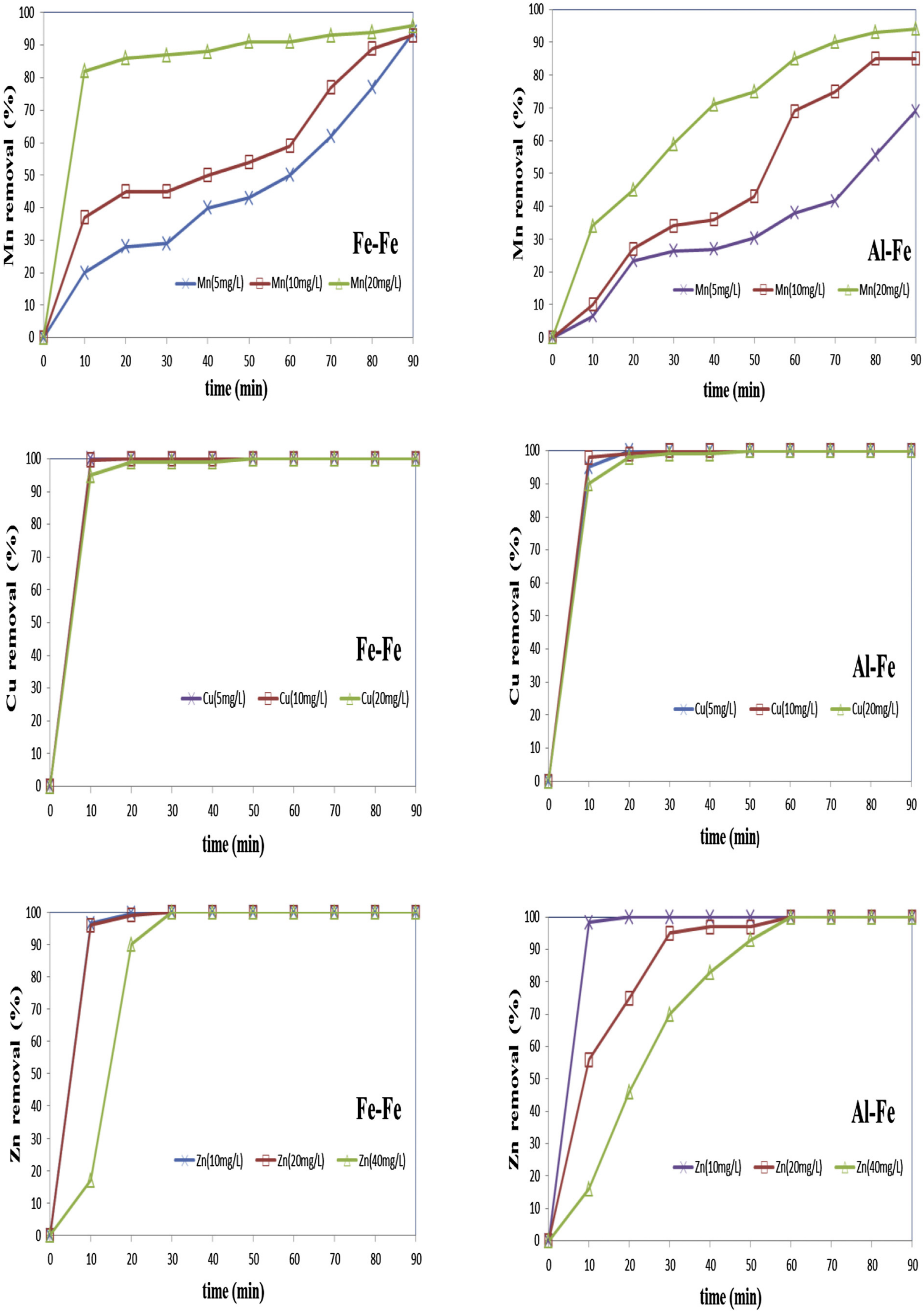

Fig. 5. Effect of initial concentration of Mn, Cu and Zn on their removal percentages, using Fe–Fe and Al–Fe electrode system and applied current 0.3 A.

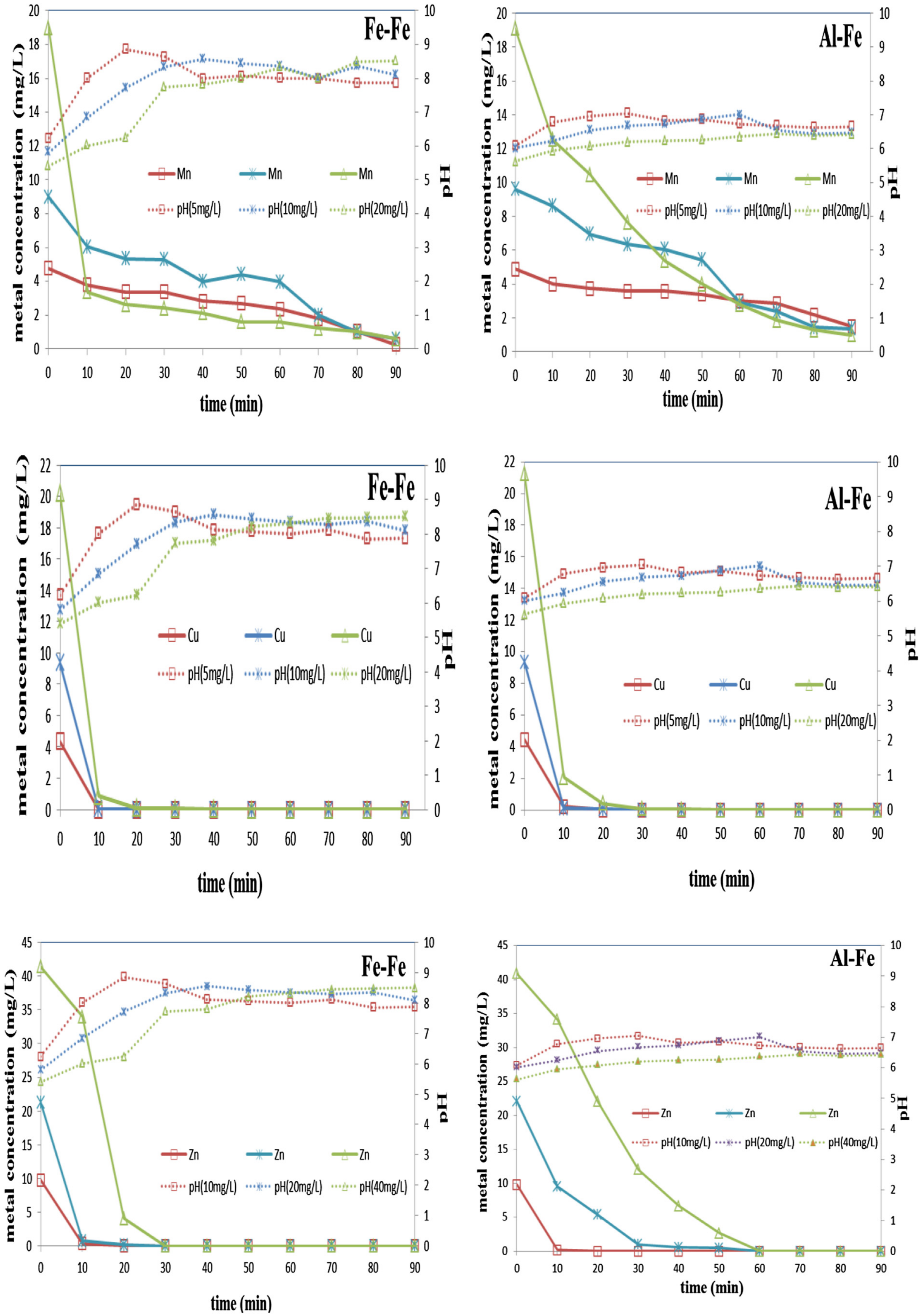

Fig. 6. Profile of Mn, Cu and Zn concentrations along with pH values over electrocoagulation time for applied current 0.3 A.

Table 5
Residual metal concentrations (mg/L), metal removal (%), removal rates (μmol/A s) of Mn, Cu and Zn, anode mass loss, final pH and energy consumption for different initial metal concentrations after 90 min of EC process, at initial pH 6, by using Fe–Fe and Al–Fe electrode system at 0.3 A.

	Fe–Fe			Al–Fe		
Initial metal concentration	C[a]	2C	4C	C	2C	4C
Residual metal concentration (mg/L)						
Mn	0.27 ± 0.008	0.61 ± 0.02	0.61 ± 0.01	1.49 ± 0.05	1.36 ± 0.06	1.09 ± 0.04
Cu	0	0	0	0	0	0
Zn	0	0	0	0	0	0
Removal (%)						
Mn	94	93	97	69	85	94
Cu	100	100	100	100	100	100
Zn	100	100	100	100	100	100
Removal rate (μmol A^{-1} s^{-1})						
Mn	7.79	15.15	21.16	5.92	17.45	32.95
Cu	3.73	8.05	17.95	3.98	8.11	19.85
Zn	8.39	18.30	58.52	8.26	27.38	70.20
Anode mass loss (g)	0.86	0.49	0.73	1.53	1.56	1.72
End pH	7.87	8.1	8.51	6.65	6.47	6.42
Energy consumption (kWh/m^3)	25.2	22.1	21.6	5.4	5.85	5.85

[a] Where C is the initial concentration of the examined metal in the real industrial wastewater (approximately 5 mg/L Mn, 5 mg/L Cu and 10 mg/L Zn).

involve the following: a) EC can be applied sufficiently for the removal of toxic metals with high removal percentages, b) an increase in the initial pH affects positively the EC process and the removal of toxic metals (Heidmann and Calmano, 2010; Shafaei et al., 2010; Hanay and Hasar, 2011; Al Aji et al., 2012), c) the removal rate and removal percentages of Cu and Zn are greater than the related of Mn (Hanay and Hasar, 2011; Al Aji et al., 2012) and d) increasing the current supply leads to acceleration of the removal process, thereby the residual metal concentrations are decreased (Heidmann and Calmano, 2008a, 2010; Shafaei et al., 2010; Shafaei et al., 2011; Al Aji et al., 2012).

In contrast with previously studies, the following statements can be made by the present work: a) the remediation of the real industrial wastewater used by Shafaei et al. (2011) led to a relatively slow removal rate of Mn (39% removal after 60 min of EC treatment) a fact that could possibly be attributed to the presence of several organic compounds in the solution and b) Heidmann and Calmano (2010), when comparing the electrode combinations, came to the conclusion that using Fe at the anode is less energy consuming than using Al.

4. Conclusions

In the present work, the efficiency of EC was investigated for the removal of Mn, Cu and Zn from a real industrial wastewater with Fe and Al electrodes. The results obtained were very encouraging and showed that EC can be successfully applied for the treatment of real wastewaters. Several parameters were examined and calculated to determine the optimal conditions under which EC performs best in treating the examined wastewater. Such parameters involved combinations of electrodes and distance between them, initial metal concentrations, applied current and initial pH of the solution, for a 90 min EC treatment.

According to the results, Mn was removed slower than Cu and Zn and its residual concentration was found higher than the other metals. All tested electrode combinations (Fe–Fe, Fe–Al, Al–Fe,

Table 6
Removal efficiency of Mn, Cu and Zn reported in literature data after EC treatment of various types of wastewaters.

	Wastewater type	Electrode combination	Initial parameters				t (min)	Results		
			Applied current and/ or current density	pH	Examined metals and/or ions	C_0 (mg/L)		Residual concentrations and/ or removal percentages		
Heidmann and Calmano (2008b)	Synthetic	Al x 4	1 A	Cu: 6 Zn: 7	$\underline{\mathrm{Zn}}^{2+}$, $\underline{\mathrm{Cu}}^{2+}$, Ni^{2+}, Ag^{+}	Cu: 50 Zn: 50	Cu: 5 Zn: 5	Cu: 100%	Zn: 100%	
Shafaei et al. (2010)	Synthetic	Al–Al	6.2 mA/cm^2	6	$\underline{\mathrm{Mn}}^{2+}$	Mn: 100	30			Mn: ~75%
Heidmann and Calmano (2010)	Galvanic	Fe–Al	Fe – 0.2 A Al – 1.5 A	5	Ni, $\underline{\mathrm{Cu}}$, Cr	Cu: 1600	180	Cu: 6.5 mg/L		
Hanay and Hasar (2011)	Synthetic	Al x 4	15 mA/cm^2	3	$\underline{\mathrm{Cu}}^{2+}$, $\underline{\mathrm{Mn}}^{2+}$, $\underline{\mathrm{Zn}}^{2+}$	Cu: 50–200 Mn: 50–200 Zn: 50–200	Cu: 5 Zn: 5 Mn: 35	Cu: 100%	Zn: 100%	Mn: 80–85 %
Shafaei et al. (2011)	a) Synthetic	Al–Al	6.2 mA/cm^2	7	$\underline{\mathrm{Mn}}^{2+}$, Co^{2+}	Mn: 25	40			Mn: > 98%
	b) Real	Al–Al	6.2 mA/cm^2	4.67	$\underline{\mathrm{Mn}}^{2+}$, Co^{2+}	Mn: 22.5	60			Mn: 39.6%
Al Aji et al. (2012)	Model	Fe x 6	25 mA/cm^2	5.5	$\underline{\mathrm{Cu}}$, Ni, $\underline{\mathrm{Zn}}$, $\underline{\mathrm{Mn}}$	Cu: 250 Mn: 250 Zn: 250	50	Cu: > 96%	Zn: > 96%	Mn: 72.6%
Mansoorian et al. (2014)	Real	Fe–Fe	6 mA/cm^2	2.8	Pb, Zn	Zn: 3.2	30		Zn: 95.2%	
Akbal and Camci (2011)	Real	Fe–Al	10 mA/cm^2	3	Cu, Cr, Ni	Cu: 45	20	Cu: 100%		
Present study	Real	Fe–Fe	0.1 A	6	Cu, Mn, Zn	Cu: 5 Mn: 5 Zn: 10	90	Cu: 100%	Zn: 100%	Mn: 89%

The elements that have been reported in literature (other studies) and are the same with the ones examined in the present study have been underlined for quick tracking and comparison.

Al–Al) led to high removal percentages for all three examined metals (almost 100%) at the highest examined applied current. The increase of current intensity accelerated the removal process, dropped off the residual metal concentrations and increased the energy consumption of the EC process. The increase of the initial concentration did not affect maximum metal removal percentages, even though the total amount of each removed metal was higher. The best results, regarding EC efficiency and energy consumption, were observed with the highest examined pH values (initial pH of the wastewater), and the lowest distance between electrodes (2 cm). Taking, also, into consideration the energy expenditure, the best result was obtained with a combination of iron electrodes (Fe–Fe), placed at 2 cm distance, at a current of 0.1 A and initial pH = 6. After 90 min of treatment, the total removals reached 89% for Mn (Mn residual concentration was found 0.52 mg/L) and 100% for Cu and Zn, at an energy consumption of 2.55 kWh/m^3.

To the authors best knowledge, the existing literature concerning the removal of toxic metals from a real industrial wastewater via EC is limited, thus this field of interest requires further investigation. The present work is merely a first step towards this direction. Furthermore, a great deal of research should be done on the interaction of TPHs or PAHs (naturally existing in real industrial wastewaters) with metal ions (Baker and Head-Gordon, 2010) and any effects (positive or negative) this could, possibly, have on the overall efficiency of the EC process.

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