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Heavy metal ions removal from metal plating wastewater using electrocoagulation: Kinetic study and process performance

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HIGHLIGHTS

- High removal of heavy metal ions from metal plating wastewater using EC treatment.
- Pseudo first-order kinetic model describes heavy metal ions removal adequately.
- Electrocoagulation time and DC current density are the key parameters in EC process.
- Metal plating wastewater treatment by electrocoagulation is economically rewarding.

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ABSTRACT

The main objective of the present study was the removal of heavy metal ions, namely Cu^{2+}, Cr^{3+}, Ni^{2+} and Zn^{2+}, from metal plating wastewater using electrocoagulation technique. An electro-reactor was used with six carbon steel electrodes of monopolar configurations. Three of the electrodes were designated as cathodes meanwhile the other three as anodes. The results showed that the removal efficiency of heavy metal ions increases with increasing both electrocoagulation (EC) residence time and direct current (DC) density. Over 97% of heavy metal ions were removed efficiently by conducting the EC treatment at current density (CD) of 4 mA/cm^2, pH of 9.56 and EC time of 45 min. These operating conditions led to specific energy consumption and specific amount of dissolved electrodes of around 6.25 kWh/m^3 and 1.31 kg/m^3, respectively. The process of metal plating removal using EC consumes low amount of energy, making the process economically feasible and possible to scale up. Moreover, the kinetic study demonstrated that the removal of such heavy metal ions follows pseudo first-order model with current-dependent parameters.

1. Introduction

Metal plating industry is one of the major chemical processes that discard large amounts of wastewaters. These industrial wastewaters contain various types of harmful heavy metals and toxic substances such as chromium, nickel, copper, zinc, cyanide and degreasing solvents [1]. Numerous approaches such as physical, chemical and biological processes including adsorption, biosorption, precipitation, ion-exchange, reverse osmosis, filtration and other membrane separations are employed to treat wastewaters [2]. Precipitation of heavy metals in an insoluble form of hydroxides is the most effective and economical method to treat heavy metals wastewater. The main idea of precipitation method is to adjust the pH of wastewater and to add chemical coagulants like aluminum or iron salts to remove pollutants as colloidal matter [3]. The precipitation typically occurs according to the following reaction:

$$M^{+n}_{(aq)} + nOH^{-}_{(aq)} \leftrightarrow M(OH)_{n(s)} \quad (1)$$

Although the chemical coagulation technique is considered to be effective in treating industrial wastewater effluents, it has quite high cost. On the other hand, the addition of chemical coagulants to the wastewater may produce side-products that are considered as secondary pollutants [4]. Alternatively, electrocoagulation (EC)

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was found to be an effective technique for precipitating industrial wastewater pollutants [5,6]. The simplicity of EC operation, low energy consumption, high quality effluent, low sludge formation and low dissolved solids made electrocoagulation a desirable treatment method [5,7,8].

In electrocoagulation process, no chemicals are added to form coagulant agents. Basically, wastewater solution is subjected to a direct electrical (DC) current field through sacrificial electrodes (cathodes and anodes) that are generally made of iron or aluminum [1,5,6]. Though it is traditional to use solid flat electrodes, cylindrical perforated ones are adopted in some previous studies to have better distribution of the applied DC field onto the wastewater treated [9,10]. Due to electrical potential difference between cathodic and anodic electrodes in electrocoagulation, water is oxidized to produce hydrogen ions (H^+) and oxygen gas and the metal oxidation will generate its cations. Simultaneously, water reduction occurs at the cathode to generate hydroxyl ions (OH^-) and hydrogen gas. For iron-iron electrodes, as in the present study, two ferric hydroxides, $Fe(OH)_2$ and $Fe(OH)_3$ are produced according to the following electrolytic reactions [11,12]:

$$Fe_{(s)} \leftrightarrow Fe^{2+}_{(aq)} + 2e^- \quad (2)$$

$$2H_2O_{(l)} + 2e^- \leftrightarrow H_{2(g)} + 2OH^-_{(aq)} \quad (3)$$

$$Fe^{2+}_{(aq)} + 2HO^-_{(aq)} \leftrightarrow Fe(OH)_{2(s)} \quad (4)$$

$$\underline{\text{Overall :}}\ Fe_{(s)} + 2H_2O_{(l)} \leftrightarrow Fe(OH)_{2(s)} + H_{2(g)} \quad (5)$$

$$4Fe_{(s)} \leftrightarrow 4Fe^{2+}_{(aq)} + 8e^- \quad (6)$$

$$8H^+_{(aq)} + 8e^- \leftrightarrow 4H_{2(s)} \quad (7)$$

$$4Fe^{2+}_{(aq)} + 10H_2O_{(l)} + O_{2(s)} \leftrightarrow 4Fe(OH)_{3(s)} + 8H^+_{(aq)} \quad (8)$$

$$\underline{\text{Overall :}}\ 4Fe_{(s)} + 10H_2O_{(l)} + O_{2(s)} \leftrightarrow 4Fe(OH)_{3(g)} + 4H_{2(s)} \quad (9)$$

The generated ferric hydroxide flocs serve as coagulant agents that can precipitate various wastewater pollutants. It is reported that Fe(III) hydroxide coagulants are more effective than Fe(II) hydroxide due to the higher stability of $Fe(OH)_3$ [13]. There are many physiochemical phenomena involved in electrocoagulation that can be summarized as [6]: (i) anodic oxidation and cathodic reduction, (ii) generation and migration of flocculating agents in the aqueous phase (iii) coagulation and adsorption of pollutants on flocculating agents and (iv) electroflotation or sedimentation of coagulated aggregates. In order to achieve optimal treatment effectiveness, the chemical/physical properties of wastewater must be monitored during the EC operation.

Electrocoagulation has been successfully applied for the treatment of different types of wastewater generated from municipal wastewater [4,10], pulp and paper mill industries [12,14], olive mills [15], textile processing [16], potato chips manufacturing [17], baker's yeast production [18] and pigments industries [13,19]. Several studies have proved the high efficiency of electrocoagulation in the removal of heavy metal ions from industrial/synthesis wastewater [1,20–22]. Unlike these studies, the present work investigated simultaneous removal of chromium (Cr^{3+}), copper (Cu^{2+}), nickel (Ni^{2+}) and zinc (Zn^{2+}) ions from metal plating wastewater using electrocoagulation (EC) technique. In addition, a kinetic study was conducted for the first time to describe the removal rates of heavy metal ions. The impact of EC time, direct current density, pH and electrical conductivity (σ) on the heavy metal ions removal by electrocoagulation was investigated. Finally, the consumption levels of both electrical energy and electrode material were assessed at different operating conditions to demonstrate qualitatively the cost-effective features.

2. Materials and methods

2.1. Experimental setup

Fig. 1 shows the schematic diagram of the electrocoagulation (EC) laboratory scale setup. The EC reactor was constructed from Pyrex glass with dimensions of 120 mm × 112 mm × 89 mm. Iron (carbon steel) plates were used as sacrificial electrodes, arranged in monopolar configurations. Six electrodes were positioned vertically with spaces of 15 mm. Three plates were connected as cathodes and the other three as anodes. The plates have rectangular geometry with the dimensions of 45 mm × 53 mm × 3 mm. The total effective surface area of electrodes immersed in wastewater solution was around 247.5 cm^2. The electrodes were connected to a direct current (DC) power supply providing voltage in the range of 0–30 V and electrical current in the range of 0–6 A. During electrocoagulation experiments, the solution was agitated continuously using mechanical mixer (Stuart Scientific, UK) with rotational speed of about 1000 rpm.

2.2. Experimental procedure

The metal plating wastewater samples were collected from the Union Locks Company/Sayegh Group located in the region of Abu-Alanda, Amman, Jordan. The physical and chemical characteristics of the metal plating wastewater used in this study are listed in Table 1. The EC reactor shown in Fig. 1 was filled with nearly 600 ml of the wastewater solution to run out the electrocoagulation experiments. The DC was adjusted to give the desired current density (CD) which is defined as the ratio of the applied direct current to the total effective surface area of electrodes. After each experiment, the EC reactor was rinsed with diluted HCl, followed by frequent distilled water washes. Before analyzing the concentrations of the heavy metal ions, the original and treated

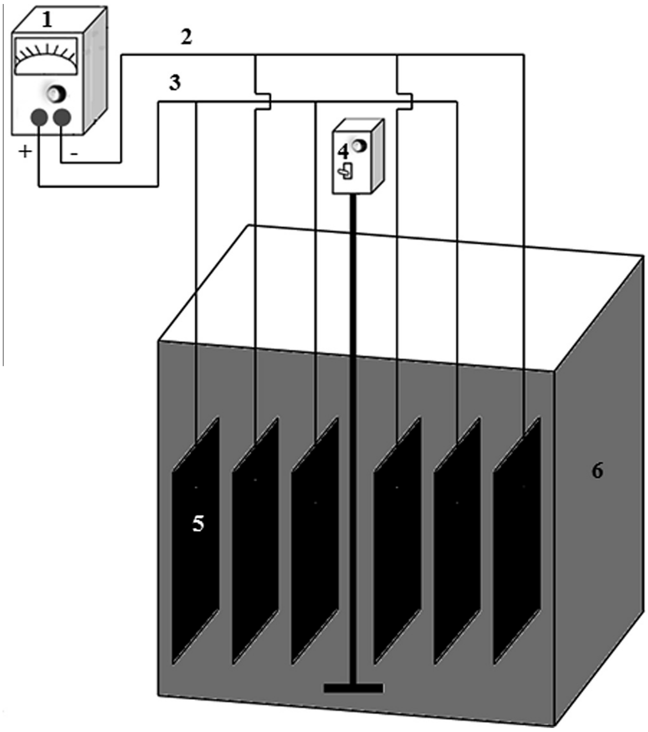

Fig. 1. Schematic diagram of experimental setup: (1) DC power supply; (2) cathode; (3) anode; (4) mechanical stirrer; (5) carbon steel electrodes; (6) EC reactor.

Table 1
Some chemical/physical characteristics of metal plating wastewater obtained from Union Locks Company/Sayegh Group located in Abu-Alanda zone, Amman, Jordan.

Parameter	Unit	Value
pH	–	9.6 ± 0.3
Cr^{3+}	ppm	93.2 ± 2.2
Cu^{2+}	ppm	33.3 ± 1.1
Ni^{2+}	ppm	57.6 ± 1.2
Zn^{2+}	ppm	20.4 ± 0.8
Electrical conductivity (σ)	ms/cm	8.9 ± 0.2
Color	–	Yellow

wastewater was filtrated using filtration papers (0.45 μm, Millipore, USA). Samples of the filtrate were taken to measure Cr^{3+}, Cu^{2+}, Ni^{2+} and Zn^{2+} ions concentrations using atomic absorption spectrophotometer. Lamotte (CON 6) conductivity meter (Model 4071) was employed to determine the electrical conductivity (σ) of wastewater. In addition, the pH of wastewater was adjusted to the desirable value using either 0.1 M NaOH or 0.1 M H_2SO_4. All experimental runs were carried out at the ambient temperature of around 26 ± 1 °C. Each experiment was performed in triplicate to rule out the uncertainty in the measurements.

3. Results and discussion

The heavy metal ions removal was measured in terms of percent removal efficiency defined as:

$$\eta\ (\%) = 100\frac{C_0 - C}{C_0}\% \tag{10}$$

where C_0 and C are the concentrations of Cr^{3+}, Cu^{2+}, Zn^{2+} or Ni^{2+} in the original wastewater sample and in the treated one at the given EC time (t), respectively.

3.1. Effect of electrical conductivity on the removal of heavy metal ions

It is well known that electrical conductivity is a key parameter that significantly affects heavy metal ions removal from wastewater using electrocoagulation process. This was supported by the study of Akbal et al. [1] for the removal of copper, chromium and nickel heavy metal ions from metal plating wastewater using EC process. They found that the removal efficiency was strongly increased with increasing electrical conductivity from 2 (original wastewater) to 6 mS/cm. However in the present study, the effect of electrical conductivity on the removal of Cr^{3+}, Cu^{2+}, Zn^{2+} and Ni^{2+} was not noticeable when the electrical conductivity increased from 8.9 mS/cm (original wastewater) to 12.0 mS/cm using sodium chloride salt as shown in Table 2. This leads to the conclusion that there is no need to adjust the electrical conductivity of metal plating wastewater above 8.9 mS/cm in order to enhance the EC performance. This result confirms that the contribution of electrical conductivity on EC performance seems to be negligible at high levels which explains the disagreement between the trend of this study and the corresponding one reported by Akbal et al. [1].

Table 2
Heavy metal ions removal efficiencies at different electrical conductivities (σ) after one-hour of EC treatment of metal plating wastewater with CD = 4 mA/cm^2, solution volume = 600 ml and pH = 9.6.

σ (mS/cm)	η_{exp} (%)			
	Cr^{3+}	Cu^{2+}	Ni^{2+}	Zn^{2+}
8.9 (original wastewater)	100	99	98	99
10.3	100	100	99	100
11.1	99	99	98	99
12.0	100	99	98	99

3.2. Effect of pH on the removal of heavy metal ions

Previous studies have reported strong dependency between the performance of electrocoagulation and the pH of wastewater [1,10,12,20–23]. Therefore, the influence of the pH upon the heavy metal ions removal from metal plating wastewater was investigated. The initial pH of the original metal plating wastewater was 9.56; see Table 1. Three pH values: 6.56, 7.89 and 10.68 were considered. Fig. 2 shows the impact of pH variations on the removal efficiencies of heavy metal ions with and without electrocoagulation. Fig. 2(a) illustrates the effect of pH on the removal efficiency of Cr^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions from wastewater samples without electrocoagulation. For such samples, Fig. 2(a) shows no significant effect of pH on the removal of copper and nickel ions. However, the removal efficiencies of chromium ions were 46% and 10% at pH = 6.56 and 10.68, respectively. At pH = 6.56, the removal efficiency of zinc ions was 38% and it was negligible at pH = 10.68. Hence, it can be concluded that the precipitate formed in metal plating wastewater of nearly neutral pH has the potential to remove $Cr^{3+}$and Zn^{2+} heavy metal ions effectively.

In fact, the dependency of heavy metals ions removal on pH will differ when EC technique is applied. In order to understand the different reaction mechanisms that may occur when iron is used as electrodes in the designed EC process, the theory of electrocoagulation by iron anode needs to be highlighted. Many researchers reported the reaction mechanisms that occur in electrocoagulation

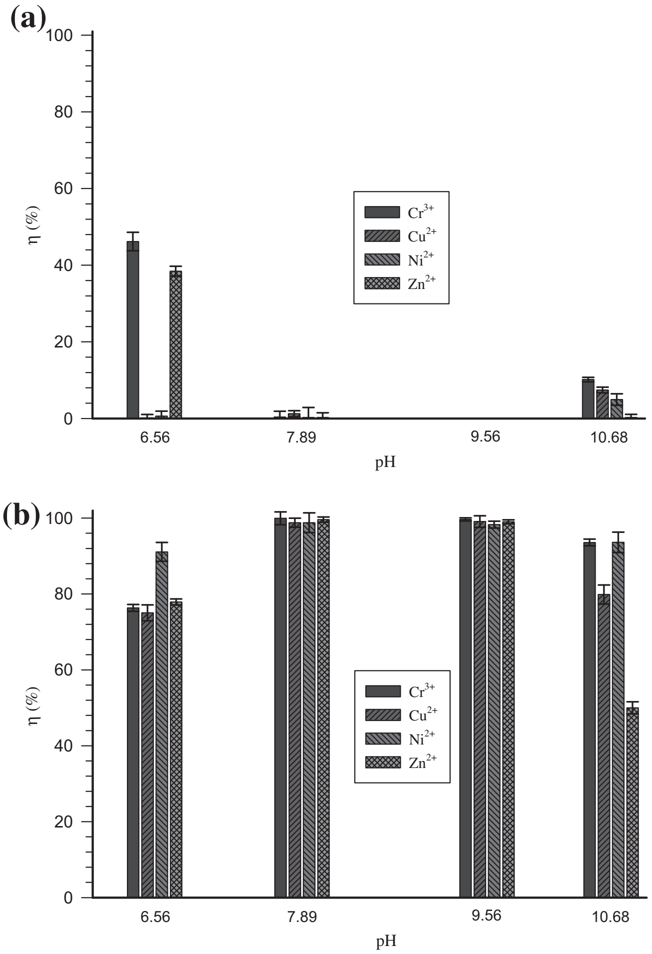

Fig. 2. Variations of removal efficiencies of heavy metal ions with pH: (a) without electrocoagulation; (b) with one-hour EC treatment under applied current density of 4 mA/cm^2. The metal plating wastewater volume is 600 ml and its σ = 8.9 mS/cm.

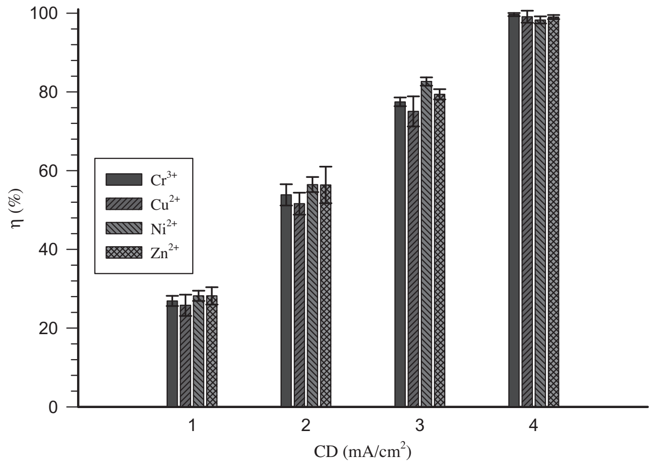

Fig. 3. Variations of the removal efficiencies of heavy metal ions with direct current density after one-hour EC treatment of 600 ml metal plating wastewater (pH = 9.6 and σ = 8.9 mS/cm).

with iron [5,23–24]. It is recommended to refer to the study reported by Moreno-Casillas et al. [23] in which they described in details the mechanisms of different reactions at different pH together with a description of the solution's color changes.

Accordingly, Fig. 2(b) presents the pH effect on metal ion concentrations and their removal efficiencies after one-hour of EC treatment with DC = 4 mA/cm^2. It is clear in the figure that the maximum removal efficiencies for all heavy metal ions occur at pH = 7.89 and 9.56. Lower removal efficiencies were obtained at pH = 6.56 and 10.68. This indicates that the heavy metal ions removal decreases in lower acidic and higher basic mediums. In alkaline medium, the oxidation of hydroxyl ions at the anode and the formation of $Fe(OH)^{4-}$ and $Fe(OH)_6^{3-}$ anions lowered the removing capacity [5]. In strongly acidic medium, the protons in the solution were reduced to hydrogen gas at the cathode and the same proportion of hydroxyl ions could not be produced [5]. In addition, the pH affects the EC performance through varying the solution physiochemical properties, such as the solubility of metal hydroxides and the electrical conductivity, and the size of colloidal particles of iron (III) complexes that are strongly reactive agents with the heavy metal ions [19,24].

3.3. Effect of current density on the removal of heavy metal ions

The effect of CD variation on heavy metal removal was investigated by running the EC experiments at different direct current fields with CD of 1, 2, 3 and 4 mA/cm^2. It was clearly observed that increasing the current density led to a significant removal of heavy metal ions concentrations. Fig. 3 shows the heavy metal ions removal efficiencies after one-hour of EC treatment at different current densities. It is clear that the removal efficiency has values in the ranges of $\eta = 23–29\%$, 52–62%, 75–83% and 98–100% for applied CD of 1, 2, 3 and 4 mA/cm^2, respectively. In other words, the current density represents a key parameter in enhancing heavy metal ions removal. This can be attributed to the direct proportionality between direct current field and potential electrolysis which implies more release of ferric ions, and thereby more generation of iron hydroxides necessary to form coagulants [16,17].

3.4. Effect of EC time and kinetic study

In this work, the kinetic study for the removal of heavy metal ions was considered for various current densities at the ambient temperature and constant wastewater volume (600 ml). For such EC batch process, the mass conservation of heavy metal ion is:

$$-\frac{dC}{dt} = (-r_D) \tag{11}$$

where $(-r_D)$ is the removal rate of heavy metal ion in ppm/min and t is the electrocoagulation (EC) time in min. First-order, second-order and pseudo first-order models were tested to describe the removal rate equations [25,26]. With the first-order model $(-r_D = k_1C)$, the integration of Eq. (11) at the initial concentration $C(0) = C_0$, gives:

$$C(t) = C_0 e^{-k_1 t} \tag{12}$$

where k_1 is the first-order rate constant in min^{-1}. For the second-order model $(-r_D = k_2C^2)$, the time-dependent concentration is obtained as:

$$\frac{1}{C(t)} = \frac{1}{C_0} + k_2 t \tag{13}$$

where k_2 is the second-order rate constant in ppm^{-1}min^{-1}. In addition, when pseudo first-order model, $-r_D = k^{app}(C - C_e)$, is prevailed, the integration of Eq. (11), gives:

$$C(t) = C_e + (C_0 - C_e)e^{-k^{app} t} \tag{14}$$

Table 3
Predicted parameters of first- and second-order removal rates of heavy metal ions at different current densities with solution volume = 600 ml, pH = 9.6 and σ = 8.9 mS/cm.

Heavy metal	CD (mA/cm^2)	First-order model $-dC/dt = k_1C$ k_1 (min^{-1})	R^2 (–)	Second-order model $-dC/dt = k_2C^2$ k_2 (ppm^{-1}min^{-1})	R^2 (–)
Cr^{3+}	2	0.0114	0.7476	0.0002	0.8283
	3	0.0218	0.7686	0.0006	0.8904
	4	0.0856	0.6619	0.0616	0.8228
Cu^{2+}	2	0.0123	0.9338	0.0006	0.9627
	3	0.0246	0.9487	0.0017	0.9720
	4	0.0787	0.9772	0.0465	0.7043
Ni^{2+}	2	0.0133	0.6696	0.0004	0.7573
	3	0.0281	0.8219	0.0015	0.9248
	4	0.0671	0.9565	0.0168	0.9177
Zn^{2+}	2	0.0116	0.6855	0.001	0.7669
	3	0.0263	0.8150	0.0036	0.8783
	4	0.0763	0.9294	0.0723	0.7753

Table 4
Predicted parameters of pseudo first-order removal rates of heavy metal ions at different current densities with solution volume = 600 ml, pH = 9.6 and σ = 8.9 mS/cm.

Heavy metal	CD (mA/cm^2)	Pseudo first-order model -dC/dt = $k^{app}(C - C_e)$		R^2 (–)
		k^{app} (min^{-1})	C_e (ppm)	
Cr^{3+}	2	0.0939	43.89	0.9859
	3	0.1165	22.52	0.9933
	4	0.2740	00.33	0.9991
Cu^{2+}	2	0.0504	16.00	0.9823
	3	0.0539	08.10	0.9866
	4	0.0560	00.31	0.9921
Ni^{2+}	2	0.1224	22.53	0.9965
	3	0.0983	09.82	0.9998
	4	0.1180	01.73	0.9939
Zn^{2+}	2	0.1168	09.02	0.9972
	3	0.0878	03.81	0.9980
	4	0.0928	00.16	0.9949

where k^{app} is the apparent pseudo first-order rate constant in min^{-1} and C_e is the equilibrium concentration. The pseudo first-order model was first proposed by Legergen [26] in which the adsorption rate is directly proportional to the concentration difference at time t and at equilibrium. Obviously, if the equilibrium concentration has zero value, the pseudo first-order model gets back to the first-order model.

Least-square method was used in order to determine the best values of the kinetic parameters [27]. The sum of squared errors (SSE) was minimized for each heavy metal ion. Concentrations of seven EC experiments (EC time = 5, 10, 15, 20, 30, 45 and 60 min) were incorporated to build the SSE objective function. The squared-correlation coefficient, R^2, was used to measure the goodness of the kinetic model. Furthermore, graphical comparison between the experimental and the corresponding predicted concentrations was depicted.

The kinetic parameters of both first- and second-order models together with the R^2 values are given in Table 3. At current density of 2 mA/cm^2, the R^2 values that correspond to both kinetic models were found to be far from unity for Cr^{3+}, Ni^{2+} and Zn^{2+}. Hence, neither first-order nor second-order kinetic model can describe the removal rate of these heavy metal ions (Cr^{3+}, Ni^{2+} and Zn^{2+}). The copper ions were the only heavy metal ions that their removal rate can be modeled by first-order kinetics since the corresponding R^2 values at all current densities were close to unity.

Table 4 presents the kinetic parameters and the correlation coefficients for pseudo first-order model at different current densities. As can be observed, all R^2 values are too close to unity. Thus, pseudo first-order kinetics can model the removal rate of all heavy metal ions adequately. On the other hand, when current density increased from 2 to 4 mA/cm^2, the apparent constant increased from k^{app} = 0.0939 to 0.274 min^{-1} for Cr^{3+} ions. For other heavy metal ions, the influence of current density, up to 4 mA/cm^2, on k^{app} was marginal. The apparent constant had an average value of around k^{app} = 0.053, 0.113, 0.099 min^{-1} for Cu^{2+}, Ni^{2+} and Zn^{2+} ions, respectively. The values of equilibrium concentrations (C_e), shown in Table 3, strongly matched the corresponding experimental ones after one-hour of electrocoagulation treatment.

Fig. 4 shows the variations of both experimental and pseudo first-order concentrations versus time at CD = 2, 3 and 4 mA/cm^2.

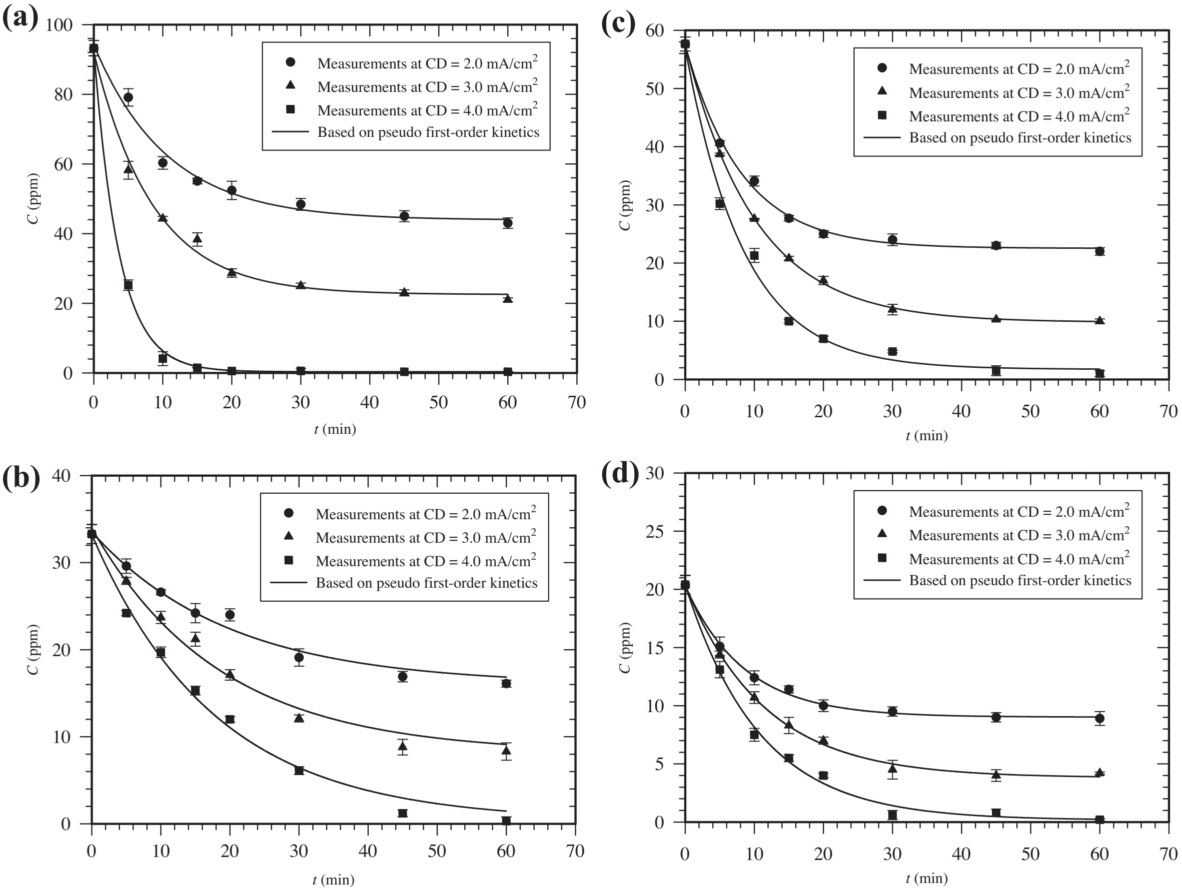

Fig. 4. Variations of heavy metal ions concentrations with EC time during electrocoagulation of 600 ml metal plating wastewater (pH = 9.6 and σ = 8.9 mS/cm) at different applied current densities: (a) Cr^{3+}; (b) Cu^{2+}; (c) Ni^{2+}; (d) Zn^{2+}.

It is clear that the pseudo first-order curves strongly fit the experimental concentrations. This also demonstrates the validity of pseudo first-order model in analyzing the removal rates of heavy metal ions. It is depicted in Fig. 4 that there is dramatic reduction in the heavy metal ion concentrations within the first 45 min. For example, after 20 min of EC treatment, the Cr^{3+} ion concentration decreased from an initial concentration of 93.2 to 52.4, 28.7 and 0.6 ppm at CD = 2, 3 and 4 mA/cm^2, respectively. However, the concentration reduction was moderately enhanced by increasing the EC time above 45 min, especially at low current densities. It is worth mentioning that at short EC time, the amount of ferric ions released from anode will not be adequate to generate iron hydroxide complexes necessary for destabilization and aggregation mechanisms involved in the electrocoagulation process [17]. Increasing the current density increased the removal rate of heavy metal ions. For example, at EC treatment of 45 min, when the current density was doubled from 2 to 4 mA/cm^2, the heavy metal ion concentrations dropped down from 45.1 to 0.3, 16.9 to 1.2, 23.0 to 1.5 and 9.0 to 0.8 ppm for Cr^{3+}, Cu^{2+}, Ni^{2+} and Zn^{2+} ions, respectively; See Fig. 4 (a)–(d).

By using pseudo first-order model, Eqs. (14) and (10), time-dependent removal efficiency can be expressed as:

$$\eta\ (\%) = 100\eta_e(1 - e^{-k^{app}t}) \tag{15}$$

where η_e is the equilibrium removal efficiency which can be calculated from Eq. (10) at equilibrium concentration.

The experimental and predicted removal efficiencies are illustrated in Fig. 5. As can be seen in Figs. 4 and 5, the decrease in the heavy metal ions concentration with EC time is accompanied by the increase in the removal efficiency. On the other hand, the treated metal plating wastewater was visually clear with around complete removal of heavy metal ions at CD = 4 mA/cm^2 after one-hour of EC treatment. This result agrees strongly with the findings of Akbal et al. [1] who reported a maximum removal efficiency of η_{max} = 100%, 100% and 99% for Cr^{+3}, Cu^{2+} and Ni^{3+} ions, respectively.

3.5. Energy and electrodes consumptions

In the electrocoagulation process, electrical energy consumption and the amount of electrode dissolved in solution exhibit significant economical factor. The electrical energy consumption per unit volume of treated wastewater was calculated using [13]:

$$E = \frac{(P)(I)(t)}{V} \tag{16}$$

where E is the specific energy consumption in kWh/m^3, P is the voltage in V, I is the DC current in A, t is EC time in hour and V is the volume of the treated wastewater in liters. The amount of electrodes dissolved per unit volume of treated metal plating wastewater, was estimated theoretically using Faraday's law:

$$m_{Fe} = 1000\frac{(I)(t) \times \mathrm{Mwt}_{Fe}}{(Z_{Fe})(F)(V)} \tag{17}$$

where m_{Fe} is the specific amount of dissolved electrode in kg/m^3, I is the direct electrical current in A, t is the EC time in seconds, Mwt_{Fe} is the molecular weight of iron (56 g/gmol), Z_{Fe} is the chemical equivalence of iron ($Z_{Fe} = 2$), F is the Faraday constant

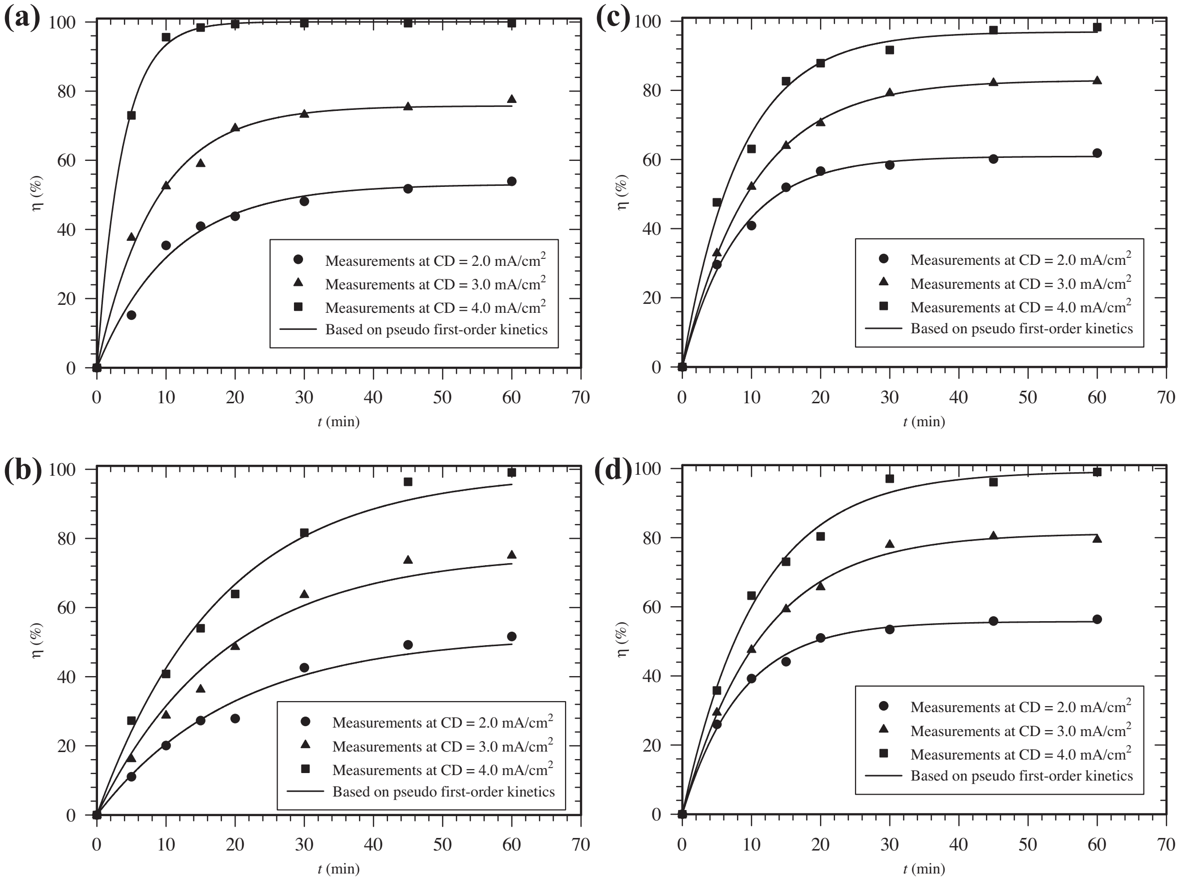

Fig. 5. Variations of removal efficiencies of heavy metal ions with EC time during electrocoagulation of 600 ml metal plating wastewater (pH = 9.6 and σ = 8.9 mS/cm) at different applied current densities: (a) Cr^{3+}; (b) Cu^{2+}; (c) Ni^{2+}; (d) Zn^{2+}.

Table 5
Removal efficiencies, amounts of electrodes dissolved and electrical energy consumptions at different current densities and EC time with solution volume = 600 ml, pH = 9.6 and σ = 8.9 mS/cm.

CD (mA/m^2)	t (min)	E (kWhr/m^3)	m_{Fe} (kg/m^3)	η_{exp} (%)			
				Cr^{3+}	Cu^{2+}	Ni^{2+}	Zn^{2+}
2	45	1.57	0.653	52	49	60	55
2	60	2.08	0.870	54	52	61	56
3	45	3.52	0.979	75	74	82	80
3	60	4.68	1.306	77	75	83	79
4	45	6.25	1.306	100	96	97	96
4	60	8.33	1.741	100	99	98	99

Table 6
Removal efficiencies of heavy metal ions from industrial/synthetic wastewater using various treatment methods.

Treatment method	C_0 (ppm)				pH	η_{exp} (%)				References
	Cr^{3+}	Cu^{2+}	Ni^{2+}	Zn^{2+}		Cr^{3+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	
Ultra filtration	50	50	50	–	7	93	98	99	–	[31]
	–	–	25	–	–	–	–	100	–	[32]
Nano-filtration	–	200	–	–	–	–	96	–	–	[29]
Reverse osmosis	167	17	26	–	7	99	99	99	–	[28]
	–	200	–	–	–	–	98	–	–	[29]
	–		21		6.5			97	–	[30]
Electrocoagulation	44.5	45	394	–	7	100	100	99	–	[1]
	93.2	33.3	57.6	20.4	9.6	100	99	98	99	This study

(F = 96500 C/mol) and V is the volume of the treated wastewater in m^3.

Table 5 summarizes the amount of dissolved electrodes and electrical energy consumption per one cubic meter of treated wastewater and the corresponding removal efficiencies at different current densities and EC treatment times. As expected, it is clear that increasing current density and/or EC time increases the removal of heavy metal ions, which is associated with increasing both the specific electrical energy consumption and the specific dissolution of electrodes. In order to maximize the removal efficiency at the operating conditions of this study, the current density must not be less than 4 mA/cm^2 and EC treatment time should be in the range of 45 to 60 min. These operating conditions minimized the specific energy consumption to the level of 6.25–8.33 kWh/m^3 and the specific amount of dissolved electrodes to the level of 1.31–1.74 kg/m^3. These consumption levels were in very good agreement with the results reported in the study of Akbal et al. [1] in which 20 min EC treatment with current density of 10 mA/cm^2 at pH = 3.0 was able to achieve removal efficiency of 100%, 100% and 99% for Cr^{3+}, Cu^{2+} and Ni^{2+}, respectively. The corresponding energy and electrode consumptions were 10.07 kWh/m^3 and 1.08 kg/m^3, respectively.

Furthermore, Table 6 gives a comparison of heavy metal ions removal efficiencies from wastewater using various treatment methods. It is obvious from Table 6 that all treatment processes achieved high removal efficiencies for all heavy metal ions considered. However, a detailed cost analysis is necessary to get a real conclusion about the feasibility of the most effective method for the heavy metal ions removal which is not the scope of the current study.

Finally, it is worth mentioning that the sludge generated in EC reactor as a byproduct might contain a wide range of components which will harm the environment if no proper management is considered. Therefore, sustainable end-use of the final sludge generated from EC reactor is an essential issue in order to minimize its negative impact on the environment. Generally, the landfill is the common used method for sludge disposal. However, sludge management and reuse became an interesting area for many researchers in the last few years, especially when the sludge contains economic compounds like metallic hydroxides as in the present study.

4. Conclusions

The present study investigated the removal of heavy metal ions from metal plating wastewater, by a batch electrocoagulation process. Electrocoagulation for long residence time with high current density significantly improves the removal of heavy metal ions. The results confirmed that the EC process is independent from electrical conductivity at high levels. In order to further minimize the energy consumption while maintaining higher removal efficiency, the current density must not be more than 4 mA/cm^2 with electrocoagulation time in the range of 45 to 60 min. Moreover, for optimal removal of heavy metal ions, the pH value of the metal plating wastewater must be adjusted to a level of slightly basic conditions.

In conclusion, EC process is an efficient treatment method for the removal of heavy metal ions from metal plating wastewater. Indeed, a continuous EC process on a pilot scale level together with a proper approach for sludge management should be first designed and characterized. In this context, a detailed careful assessment of both environmental and economic issues should be considered.

References

[1] F. Akbal, S. Camcı, Copper, chromium and nickel removal from metal plating wastewater by electrocoagulation, Desalination 269 (2011) 214–222.

[2] G. Tchobanoglous, F.L. Burton, H.D. Stensel, Wastewater Engineering: Treatment and Reuse, fourth ed., McGraw Hill, Boston, 2003.

[3] V. Agridiotis, C.F. Forster, C. Carliell-Marquet, Addition of Al and Fe salts during treatment of paper mill effluents to improve activated sludge settlement characteristics, Bioresour. Technol. 98 (2007) 2926–2934.

[4] T. Clark, T. Stephenson, Effects of chemical addition on aerobic biological treatment of municipal wastewater, Environ. Technol. 19 (1998) 579–590.

[5] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC) – science and applications, J. Hazard. Mater. 84 (2001) 29–41.

[6] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol. 38 (2004) 11–41.

[7] B. Zhu, D.A. Clifford, S. Chellam, Comparison of electrocoagulation and chemical coagulation pretreatment for enhanced virus removal using microfiltration membranes, Water Res. 39 (2005) 3098–3108.

[8] P.K. Holt, G.W. Barton, M. Wark, C.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, Colloids Surf. A 211 (2002) 233–248.

[9] K. Bani-Melhem, M. Elektorowicz, Performance of the submerged membrane electro-bioreactor (SMEBR) with iron electrodes for wastewater treatment and fouling reduction, J. Membr. Sci. 379 (2011) 434–439.

[10] M. Al-Shannag, K. Bani-Melhem, Z. Al-Anber, Z. Al-Qodah, Enhancement of COD-nutrients removals and filterability of secondary clarifier municipal wastewater influent using electrocoagulation technique, Sep. Sci. Technol. 48 (2013) 673–680.

[11] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters, J. Hazard. Mater. 129 (2012) 116–122.

[12] M. Al-Shannag, W. Lafi, K. Bani-Melhem, F. Gharagheer, O. Dhaimat, Reduction of COD and TSS from paper industries wastewater using electrocoagulation and chemical coagulation, Sep. Sci. Technol. 47 (2012) 700–708.

[13] C.A. Martınez-Huitle, E. Brillas, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review, Appl. Catal. B 87 (2009) 105–145.

[14] S. Khansorthong, M. Hunsom, Remediation of wastewater from pulp and paper mill industry by the electrochemical technique, Chem. Eng. J. 151 (2009) 228–234.

[15] Ü.T. Ün, S. Uğur, A.S. Koparal, Ü.B. Öğütveren, Electrocoagulation of olive mill wastewaters, Sep. Purif. Technol. 52 (2006) 136–141.

[16] Z. Zaroual, M. Azzi, N. Saib, E. Chainet, Contribution to the study of electrocoagulation mechanism in basic textile effluent, J. Hazard. Mater. 131 (2006) 73–78.

[17] M. Kobya, H. Hiz, E. Senturk, C. Aydiner, E. Demirbas, Treatment of potato chips manufacturing wastewater by electrocoagulation, Desalination 190 (2006) 201–211.

[18] M. Kobya, S. Delipinar, Treatment of the baker's yeast wastewater by electrocoagulation, J. Hazard. Mater. 154 (2008) 1133–1140.

[19] A. Gurses, M. Yalcin, C. Dogan, Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables, Waste Manage. 22 (2002) 491–499.

[20] C.A. Basha, N.S. Bhadrinarayana, N. Anantharaman, K.M. Begum, Heavy metal removal from copper smelting effluent using electrochemical cylindrical flow reactor, J. Hazard. Mater. 152 (2008) 71–78.

[21] I. Heidmann, W. Calmano, Removal of Zn(II), Cu(II), Ni(II), Ag(I) and Cr(VI) present in aqueous solutions by aluminum electrocoagulation, J. Hazard. Mater. 152 (2008) 934–941.

[22] N. Adhoum, L. Monser, N. Bellakhal, J.E. Belgaied, Treatment of electroplating wastewater containing Cu2+, Zn2+ and Cr (VI) by electrocoagulation, J. Hazard. Mater. 112 (2004) 207–213.

[23] H.A. Moreno-Casillas, D.L. Cocke, J.A.G. Gomes, P. Morkovsky, J.R. Parga, E. Peterson, Electrocoagulation mechanism for COD removal, Sep. Purif. Technol. 56 (2007) 204–211.

[24] M. Mollah, P. Morkovsky, J.A.G. Gomes, M. Kesmez, J. Parga, D.L. Cocke, Fundamentals, present and future perspectives of electrocoagulation, J. Hazard. Mater. 114 (2004) 199–210.

[25] Z. Al-Qodah, W.K. Lafi, Z. Al-Anber, M. Al-Shannag, A. Harahsheh, Adsorption of methylene blue by acid and heat treated diatomaceous silica, Desalination 217 (2007) 212–224.

[26] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, K. Sven. Vetenskapsakad. Handl. 24 (1898) 1–39.

[27] C. Gerald, P. Wheatley, Applied Numerical Analysis, seventh ed., Addison and Wesley, 2004.

[28] H. Ozaki, K. Sharmab, W. Saktaywirf, Performance of an ultra-low-pressure reverse osmosis membrane (ULPROM) for separating heavy metal: effects of interference parameters, Desalination 144 (2002) 287–294.

[29] H.A. Qdais, Hassan Moussa, Removal of heavy metals from wastewater by membrane processes: a comparative study, Desalination 164 (2004) 105–110.

[30] J.-J. Qin, M.-N. Wai, M.-H. Oo, F.-S. Wong, A feasibility study on the treatment and recycling of a wastewater from metal plating, J. Membr. Sci. 208 (2002) 213–221.

[31] M.A. Barakat, E. Schmidt, Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater, Desalination 256 (2010) 90–93.

[32] A. Kryvoruchko, L. Yurlova, B. Kornilovich, Purification of water containing heavy metals by chelating-enhanced ultrafiltration, Desalination 144 (2002) 243–248.