Operational Parameter Influence on Heavy Metal Removal from Metal Plating Wastewater by Electrocoagulation Process

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Among the different treatment processes available for industrial wastewater treatment, electrocoagulation represents a challenging option due to several features, such as environmental compatibility, inherent safety, energy and cost effectiveness. The effectiveness of electrocoagulation process (ECP) using aluminium and iron electrodes for the removal of heavy metals from industrial wastewater has been investigated, with particular attention to the effects of operating parameters (pH, inter-electrode distance, hydraulic retention time and current density) on removal efficiency. In the first step of the experimental phase, a laboratory-made artificial wastewater containing heavy metals (Cu, Ni and Pb) was adopted in order to identify the optimum conditions that were subsequently applied to treat a metal plating industrial wastewater. Experimental results revealed that under the optimal experimental conditions (actual pH 6.32, current density 0.026 A cm^{-2}), the removal efficiency of heavy metals from artificial wastewater was higher than 95 %.

1. Introduction

Despite the products of the process industry, which are fulfilling many daily needs, the public tolerance level for acute and environmental risks remains low (De Rademaeker et al., 2014), so that the need of more stringent constraints to minimize the impact related to heavy cation dispersions from wastewaters in different sectors (e.g., fertilizers, tanneries, pesticides, food, paper, and metal plating industries) represents a challenging problem. Industrial wastewaters released from metal plating facilities contain different types of harmful heavy metals such as copper, lead, chromium, nickel and zinc (Akbal et al., 2011). The most common treatment methods include: absorption, precipitation, ion exchange, reverse osmosis and electrocoagulation. Precipitation is considered as the most applicable and cost effective technology, even though it produces large amount of sludge requiring further treatment. Membrane process combining complexation and ultrafiltration were recently explored for chromium containing wastewater. Membrane separation, ion exchange and reverse osmosis (Reverberi et al., 2014) can also reduce metal ions effectively, but the relevant drawbacks are mainly related to their operational problems, high fixed and installation costs. For these reasons, electrocoagulation technology has been proposed as a better alternative having many advantages on these existing techniques. ECP is very versatile, environmentally compatible, safe, energy efficient and cost effective (Cotillas et al., 2014), providing the opportunity of applying inherent safety principles, in analogy with other consolidated processes (e.g. Fabiano et al., 2013), without implementing too stringent safety standard (Abrahamsen et al., 2013). Namely, "intensification" guideword is performed by the design of a more compact treatment facility and by the reduced sludge volume. "Elimination" is related to the absence of chemicals in the depuration process and connected hazards associated with inventories and possible release/accident scenario at the gaseous phase (Palazzi et al., 2013), at the liquid phase (e.g. Palazzi et al., 2012), or at the solid one (e.g. Fabiano et al., 2014). In this process, metal electrodes dissolution takes place at the anode and hydrogen gas evolution occurs at the cathode. Metallic ions generated at the anode during ECP undergo hydrolysis with further production of a series of activated intermediates destabilizing the dispersed particles in the wastewater

(Vasudevan et al., 2011). The electrochemical dissolution of iron anode is much more complex owing to the two oxidation state of iron species: Fe^{2+} (ferrous) and Fe^{3+} (ferric). Recent studies have evidenced that iron is present as Fe^{2+} which is oxidized to Fe^{3+} by dissolved oxygen and finally it hydrolyses to form the hydroxide (Al-Qodah et al., 2015). Anodic and cathodic reactions can be summarized as follows (Mollah et al., 2004):

$$Al \rightarrow Al^{3+} + 3e^- \qquad (1)$$

$$Al^{3+} + nH_2O \rightarrow Al(OH)_n^{3-n} + nH^+ \qquad (2)$$

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (3)$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad (4)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (5)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (6)$$

ECP was used successfully for different wastewater treatment. Cotillas et al., (2014) treated urban wastewater by EC-UV Irradiation Process, Drouiche et al., (2011) studied the main variables for fluoride removal from pretreated photovoltaic wastewater, Palahouane et al., (2013) optimized ECP removal of fluoride from post treated fluorinated wastewater using Al material as anode and cathode and Kabdash et al., (2009) used ECP for treating complexing agent and heavy metals removal from simulated reactive dye bath effluent. In this work, the effectiveness of ECP for removal of heavy metals from real industrial wastewater was studied by using Al and Fe electrodes. This study aims at identifying the optimum operational values for safe and effective ECP. In the first step, a synthetic wastewater containing heavy metals (Cu, Ni and Pb) was considered and investigated at lab-scale to identify optimum operating conditions in terms of pH, hydraulic retention time, current density and inter-electrode distance. In the following experimental step, the optimum operating conditions were applied to treat an industrial wastewater from a metal plating firm to verify the overall performance and assess the industrial feasibility of the process.

2. Materials and methods

The schematic diagram of electrocoagulation experimental setup is shown in Figure 1. Synthetic wastewater solutions were prepared by dissolving into tap water $CuSO_4 \cdot 5H_2O$ (0.393 gL^{-1}), $NiSO_4 \cdot 6H_2O$ (0.20 gL^{-1}) and $Pb(NO_3)_2$ (0.16 gL^{-1}). The concentrations of copper, nickel and lead in the synthetic wastewater were 105 mgL^{-1}, 110 mgL^{-1} and 63 mgL^{-1} respectively. Industrial wastewater was provided by Daeduck Electronics Co., Ltd. Korea, with a copper concentration of 55 mgL^{-1}. Al and Fe (99.5%) electrodes were connected to a DC power supply providing 0–30V (0–8 A) with current density control by a potentiostat/galvanostat. All the experimental runs were carried out at constant temperature (25 ± 1) °C. Analyses were performed following standard methods for the examination of wastewater (APHA, 2005). Atomic absorption spectroscopy (AAS) (Spectra AA/220FS-Varian) was used for the analysis of residual metal concentration. The whole set of optimum operational conditions was determined by applying a proper experimental factorial design. Data represent the average of three replicates with observed experimental error of 4%.

3. Results and discussion

3.1. Synthetic wastewater

The effects of operating parameters (pH, inter-electrode distance, hydraulic retention time, HRT, and current density, CD) on heavy metal removal efficiency were thoroughly studied by using aluminium and iron electrodes for synthetic wastewater.
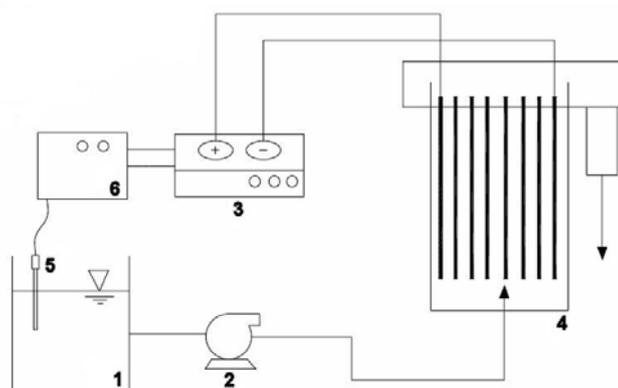
Figure 1: Schematic diagram of electrocoagulation experimental setup: 1) Raw wastewater, 2) Peristaltic pump, 3) Power supply, 4) Electrocoagulation reactor, 5) pH meter, 6) Current density controller.

As EC proceeds in liquid solution, the pH of the medium changes, exerting a considerable effect on the performance of the global process, as well as on the solubility of the analyte, according to the initial pH and electrode type. The removal efficiency varies directly for growing pH of the influent wastewater. Figure 2 illustrates the effect of pH increase on the removal efficiency. The removal efficiency of the electrocoagulation reactor was as low as 53% at a pH value of 3.11 owing to the concentration of cationic monomeric species. For pH values up to 6.13 in the solution, the removal efficiency increased to 86 % for both types of electrodes. Higher removal efficiency is due to hydroxide precipitation at cathode. Using iron electrodes, metal removal efficiency decreases when solution is acidic as the oxidation of ferrous iron (Fe II) to ferric iron (Fe III) lessens at high pH, whereas alkaline pH promotes this oxidation together with complex polymerization. In case of aluminum electrodes, cationic monomeric species Al^{3+} and $Al(OH)_2^+$ prevail at low pH, while under alkaline conditions, Al^{3+} and OH^- ions generated by the electrodes react to form various monomeric and polymeric species, e.g., $Al(OH)_2^+$, $Al(OH)_2^{2+}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, and $Al_{13}(OH)_{34}^{5+}$ which finally transform into insoluble amorphous $Al(OH)_{3(s)}$ through complex polymerization/precipitation kinetics. According to literature (Gourich et al., 2009), the formation of $Al(OH)_{3(s)}$ is optimal for pH values in the whole range [6-8]. Due to the slight influence in this range, original pH of plating wastewater represents a suitable choice, requiring no chemical addition and therefore no chemical storage in a real scale plant, consistently with hazardous inventories minimization. Inter-electrode distance reflects the influence of electrostatic field created between electrodes into the reactor on the process effectiveness. This electrostatic field exerts an inverse relationship with the distance between electrodes: when the distance between the electrodes increases, the resistance between the electrodes increases giving a lower electric current intensity in the cell. This resistance growth causes slower displacement of ions formed during the electrolysis, thus the interaction of ions with hydroxide polymers is weaker resulting in low efficiency. What has been stated is better explained by the trend of removal efficiency described in Figure 3. When the distance between electrodes is small (4 mm), the removal efficiency is at its maximum value (91 %). But as the distance between the electrodes started to increase, the removal efficiency started to decrease down to 50 % when the gap between electrodes was 24 mm. Hydraulic retention time (HRT) is a measure of the average permanence time inside the electrocoagulation reactor. This is an important factor which affects the removal efficiency of ECP. Different HRTs (20, 40, 60, 80, 100 and 120 s) were used in this experimental phase to determine the optimum value, as clearly depicted in Figure 4.
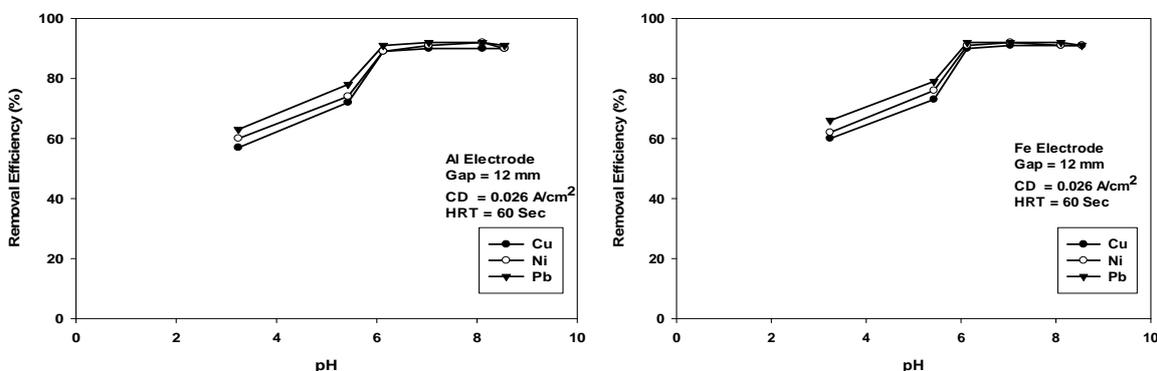
Figure 2: Influence of pH on Cu, Ni, Pb removal efficiency by ECP for Fe and Al electrodes.
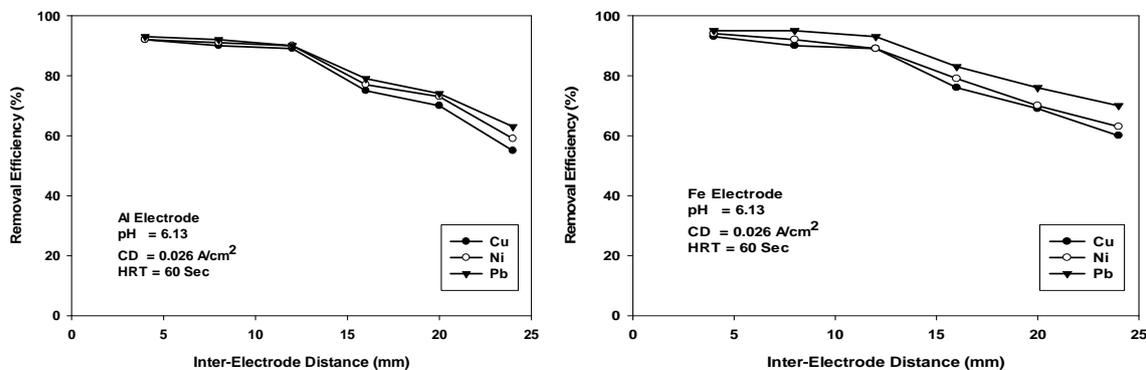
Figure 3: Influence of inter-electrode distance on Cu, Ni, Pb removal efficiency for both type of electrodes.

For longer retention time of reactor feed, the heavy metal removal efficiency increases up to an asymptotic value: at HRT of 20 s the experimental removal efficiency was 57 % but when HRT grew up to 60 s, it increased up to 90 % and further reached 96 % when HRT attained 120 s. Both type of electrodes showed removal efficiencies exceeding 90 % at higher HRT values. The current density exertss the strongest influence on the performance of all electrochemical processes. Moreover, it controls the anode dissolution speed and the hydrogen formation in the reactor. It determines the coagulant production rate (for Al^{2+}, Fe^{2+} ions released by anode) and the production of bubbles, their size and distribution. Figure 5 provides an overview of experimental runs conducted at six values of current density, namely 0.007, 0.014, 0.020, 0.026, 0.032, 0.040 (A cm^{-2}), for both types of electrodes. At a current density of 0.007 A cm^{-2}, the removal efficiency was as low as 35 %. For increasing values of the current density, the efficiency also increased and it reached 95 % when the current density was increased to 0.026 A cm^{-2} for both type of electrodes. Furthermore, the results indicated that the removal efficiency increased from 35 % to 95 % as the current density increases from 0.007 to 0.026 A cm^{-2}, owing to the higher transfer rate of Al^{3+} and Fe^{3+} ions to wastewater at higher current density and the corresponding enhancement of the generation rate of $Al(OH)_3$ and $Fe(OH)_3$ acting as adsorbents for the metal ions in wastewater (Akbal et al., 2011). A further increase in the current density yields a small increase in removal efficiency, in spite of relevant energy and electrode consumption, so that an optimum value of current density was set at 0.026 A cm^{-2}. The results illustrated in Figure 5 also describe that at a minimum value of the current density, the removal efficiency was as low as 35 % even when the other parameters were at their optimum values. However, during the whole experimental runs, when current density was at its optimum value (0.026 A cm^{-2}), the removal efficiency never dropped below 50 %.

3.2. Industrial wastewater performance

In the second phase of this study, the results from the first ECP step were applied to an industrial wastewater contaminated with copper. The concentration of copper in industrial wastewater was 55 mg L^{-1} with a pH value of 6.32. Results obtained during treatment of industrial wastewater by ECP showed a behaviour analogous to the one obtained during treatment of synthetic wastewater for both aluminium and iron electrodes as shown in Figure 6.
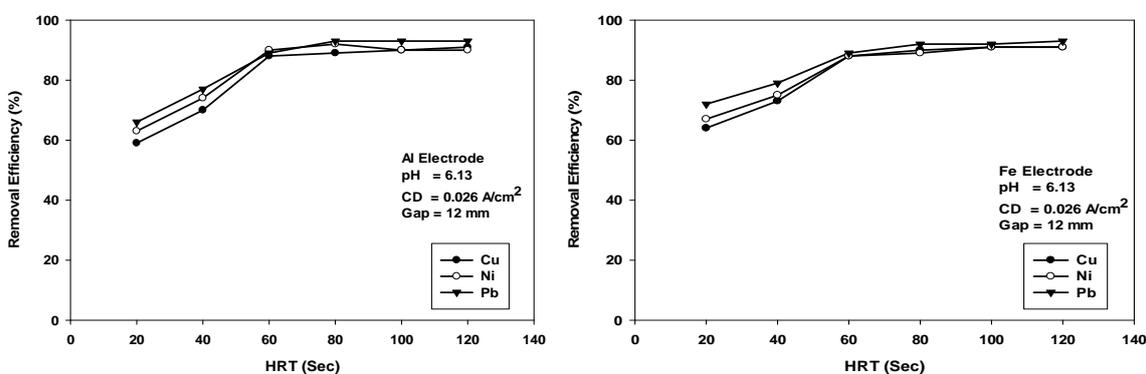
Figure 4: Influence of hydraulic retention time on Cu, Ni, Pb removal efficiency by ECP for Fe and Al electrodes.
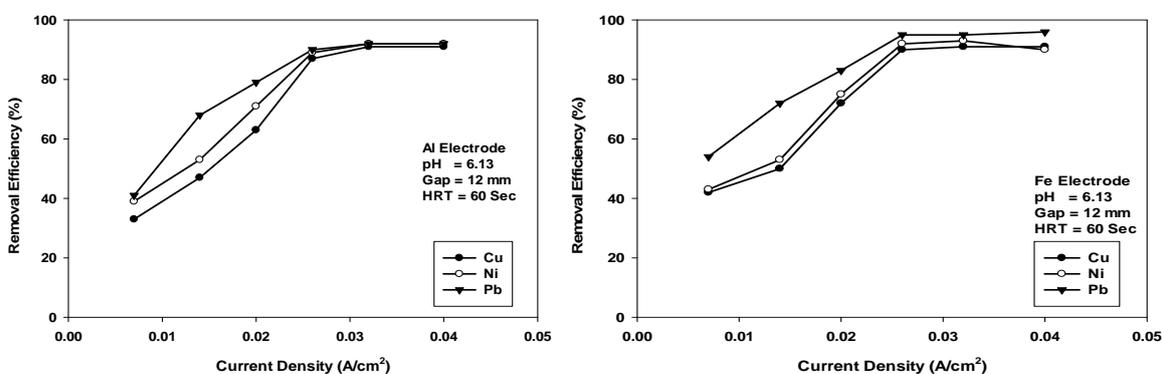
Figure 5: Influence of current density on Cu, Ni, Pb removal efficiency by ECP for Fe and Al electrodes.
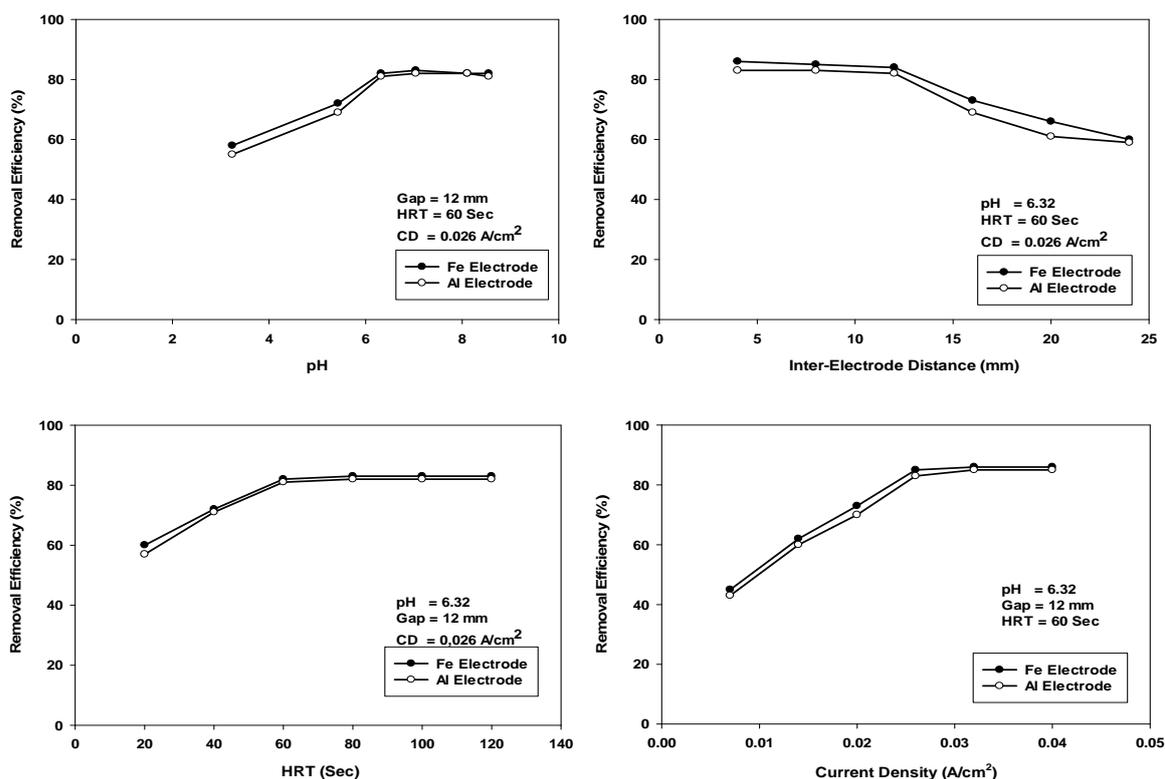
Figure 6: Cu removal efficiency as a function of different operational parameters, for metal plating wastewater.

Analogously to previous runs, pH effect was not very significant in the explored range, so that the optimum value of pH for industrial wastewater treatment can be set at the original value, to avoid the addition of any chemical for pH adjustment, consistently with "minimization" guideword. The removal efficiency recorded for industrial wastewater was slightly less than the one typical of synthetic wastewater due to the presence of other impurities/suspended particles in wastewater in addition to copper contamination. As a whole, the removal efficiency was higher than 85 % at optimum operating conditions for both types of electrodes.

3.3. Simplified kinetic approach

Finally, we present a preliminary kinetic modelling based on the approach by Al-Qodah et al, (2015):

$$-\frac{dC}{dt} = (-r_D) \tag{8}$$

$$C(t) = C_0 e^{k_1 t} \tag{9} \qquad\qquad C(t) = C_e + (C_0 - C_e)e^{-k^{app}t} \tag{10}$$

where $(-r_D)$ = heavy metal removal rate [ppm min^{-1}]; t = ECP time [min]; k_1 = first order constant, k^{app} = pseudo first-order rate constant [min^{-1}], C_0 = initial concentration; C_e = equilibrium concentration. This model becomes a first order model when the equilibrium concentration goes to zero. We used a least squares regression technique to estimate the relevant kinetic parameters. Concentrations of ECP experimental runs were incorporated to build the SSE objective function.

Table 1: First order and pseudo first order parameters at pH=6.12, Gap=12 mm, CD= 0.026 A cm^{-2}.

Heavy Metal	Electrode	First Order Model k_1	R^2	Pseudo first order Model k^{app}	R^2
Cu^{+2}	Al	0.0171	0.9381	0.0350	0.9901
	Fe	0.0177	0.9379	0.0355	0.9877
Ni^{+2}	Al	0.0190	0.9321	0.0370	0.9875
	Fe	0.0221	0.9331	0.0255	0.9386
Pb^{+2}	Al	0.0253	0.9215	0.0400	0.9700
	Fe	0.0204	0.9266	0.0355	0.9748

The correlation coefficient, R^2, was used to measure the goodness-of-fit concerning the adopted model. The kinetic parameters of both first- and pseudo first-order models together with the R^2 values are provided in Table 1, in connection with different hydraulic retention times. It can be observed that the pseudo first-order kinetics seems adequate in describing the removal rate of all heavy metal ions considered.

4. Conclusions

In this study, the effect of different operating conditions on heavy metal removal efficiency during ECP was investigated in order to determine the optimum operating conditions. The process here presented is capable of attaining high removal efficiencies for both aluminium and iron electrodes, providing as well the opportunity of eliminating hazards by elimination and intensification guidewords of inherent safety. According to a simplified kinetic approach, the process can be successfully described by a pseudo first order kinetics. At optimum operating conditions (pH=6.32, Gap= 12 mm, HRT= 60 seconds and CD= 0.026 A cm^{-2}), the removal efficiency on synthetic wastewater, which proved to be strongly affected by current density and slightly influenced by solution pH, was higher than 95 %. The main appeal of this paper consists in demonstrating the process feasibility and optimizing Fe and Al electrode set-up for the safe and effective ECP, in view of a proper scale-up for the specific industrial context.

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