

Optimization of the Electrocoagulation Process for the Removal of Lead and Copper Ions from Aqueous Solutions Using Aluminum Electrodes

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Abstract- The present work focused on the removal of lead and copper from aqueous solution on a laboratory scale using an electrochemical technique. Aluminium electrodes were used as both the anode and cathode. The various operating parameters on the removal efficiency of lead and copper were investigated, such as initial pH, applied current density (J), reaction time, solution conductivity and electrical energy consumption. The best metals removal efficiencies that could be achieved were obtained for an optimum initial pH value of 5, current density of 1.029 mA cm⁻² and a conductivity of 1.107 mS cm⁻¹. Under optimal conditions with 30 min treatment, lead and copper removal efficiency reached 91.4 and 54.1 % respectively. The obtained results showed that electrocoagulation could be regarded as a potential technique for the treatment of industrial wastewater containing heavy metal ions.

Keywords— Electrocoagulation, lead removal, copper removal, Aluminum electrodes.

I. INTRODUCTION

Introduction Water contamination of heavy metals has become a grave environmental issue [1]. Heavy metals are discharged from a variety of sources in daily life and can be readily oxidized into ions when dissolved in water. Among the heavy metals, cadmium (Cd), lead (Pb), mercury (Hg), nickel (Ni), copper (Cu), and zinc (Zn) are the most hazardous [2].

Lead has been a major focus in wastewater treatment because it is associated with many health hazards [3]. The major bio-chemical effect of Pb (II) is its interference with heme synthesis, which leads to hematological damage. Thus, it is imperative that lead is removed from effluent before being discharged into the sewage system or into the aquatic environment [4].

Lead is a priority substance in the framework of the European water policy (Water Framework Directive 2000/60/EC [5] and Water Environmental Quality Standards Directive 2008/105/EC [6]), because it presents a significant risk to biota and humans, given its persistence, toxicity and bioaccumulation characteristics [7].

Copper is an important trace element required by humans for its role in enzyme synthesis, tissues and bone development [8]. However, the divalent copper (Cu²⁺) is toxic and

carcinogenic when consumed in excess through ingestion. The excessive Cu²⁺ consumption leads to its deposition in liver and subsequent vomiting, headache, nausea, respiratory problems, abdominal pain, liver and kidney failure and finally gastrointestinal bleeding [8 -10]. It has known detrimental deleterious effects on the soil biota and damages to many plant species including some of the endemic Australian native plant species [11].

The excessive amounts of Cu²⁺ in fresh water resources and aquatic ecosystem damage the osmo-regulatory mechanism of the fresh water animals and cause mutagenesis in humans [12]. Large quantities of Cu²⁺ are released by the disposal of untreated industrial waste [11]. United State Environmental Protection Agency has set its Cu²⁺ permissible limits as 1.3 mg L⁻¹ in industrial effluent [13]. World Health Organization (WHO) defines the Cu²⁺ permissible limit of 1.5 mg L⁻¹, in drinking water [14].

Since growing populations result in significant increases in wastewater volume, there is an urgent need to develop innovative effective and inexpensive technologies to treat wastewater. To date, three major strategies are used to approach the problem of metal ion removal from water: chemical precipitation, reverse osmosis processes, and adsorbents, such as activated carbon or ion exchangers [1; 15-17]. To address this problem, technologies such as ion exchange, ultrafiltration, reverse osmosis and chemical precipitation have been developed. Each treatment method has advantages and disadvantages. Ion exchange, for example, while highly effective in removal of certain charged contaminants, requires resin regeneration or replacement at a high cost. Ultrafiltration and reverse osmosis are clean processes, but can be prohibitively expensive. While chemical precipitation is a simple process, it does generate a high volume of sludge [18].

An effective technology that meets the requirements of process cleanliness, ease of manipulation, and low operational and investment costs is electrocoagulation (EC). The electrocoagulation technologies are essentially electrolytic processes that involve the destabilization of suspended, emulsified or dissolved pollutants in an aqueous medium, by the application of an electric current. In electrocoagulation (a process similar to chemical coagulation), there is a reduction of the net surface charge to a point where the colloidal

particles can approach closely enough for Van der Waal's forces to hold them together and allow aggregation to take place [18].

The aim of the present study was to enhance the performance of electrocoagulation process to remove lead and copper by optimizing the experimental conditions, such as initial pH (pHi), electrolysis time, initial conductivity of the solution (σ_i), and current density (J).

II. MATERIALS AND METHODS

A. Electrocoagulation tests

The electrolytic cell used to conduct the experiments consists of a 1 L glass beaker. The electrodes (anode and cathode) used in this work were formed by two parallel rectangular aluminum plates (25 cm \times 8 cm \times 0.2 cm). The effective area of each electrode used was 68 cm² (8.5 cm \times 8 cm). Only one side of each electrode was taken as working surface: the second one was spared. The anode/cathode gap was kept constant at 2 cm. In order to avoid a passivation film, these electrodes were cleaned before use by treating them with NaOH and HCl aqueous solutions. A gentle agitation was made using a magnetic mixer. The applied current density was maintained at the ranges of 0 to 3 A and 0 to 30 V using a regulated direct current (DC) AFX 2930 SB DC power supply, and the voltage cell was continuously recorded. The conductivity and pH of the solution were measured during the experiments using a conductivity meter Jenway 4510 (Ω Metrohm) and a pH meter pH Cyber Scan 510 (WDW, Germany), respectively. If required, the pH of the electrolyte was adjusted with HCl or NaOH solution of 0.1 M concentration before the electrolysis started. The current intensity between the electrodes and the resulting voltage was controlled using the generator.

A schematic diagram of electrochemical cell is shown in Fig. 1.

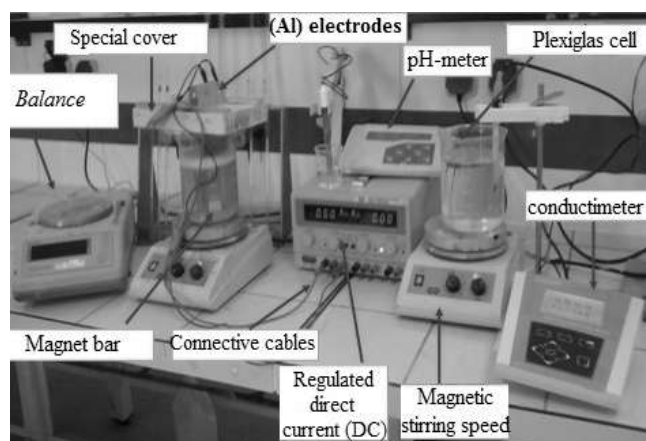


Fig. 1. Laboratory scale cell assembly.

B. Analytical method

The lead and copper concentrations were determined by atomic absorption spectroscopy with flame (AASF) method. In the context of this study, this method was the most feasible one and could be adequately adapted to higher concentration of the measurement of more than 30 elements with detection limits consistent with the objectives of the analysis of natural water. For this reason, atomic absorption spectroscopy with flame Nova 400 was used while conducting the analyses of lead and copper concentrations in water.

The performance was measured in terms of removal efficiency (% removal). The mathematical expression for their calculation was:

$$\% \text{ removal} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where: C_i = initial metal concentration (mg L⁻¹) and C_f = residual metal concentration (mg L⁻¹)

III. RESULTS AND DISCUSSION

A. Optimal pHi determination

It has been established that the pH has a considerable influence on the performance of EC process. Hence, optimization of pH for lead and copper removal was done by carrying out a series of experiments with an initial pH varying in the range of 3 to 7 for an initial Pb (II) and Cu (II) concentrations of 70 mg L⁻¹, a current density of 1.47 mA cm⁻², electrolysis time of 60 minutes and an initial conductivity of $\sigma_i = 1,175 \text{ mS cm}^{-1}$

Fig. 2 depicts the evolution of lead and copper removal as function of the initial pH.

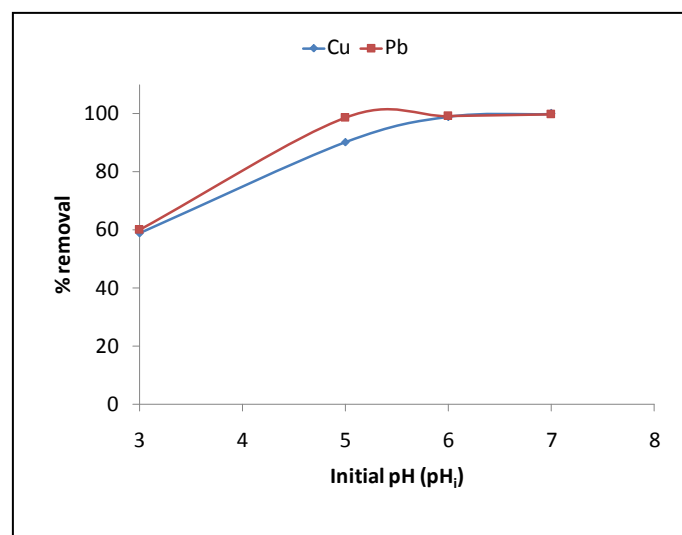


Fig. 2. Effect of initial pH on the removal of Pb (II) and Cu (II) by electrocoagulation.

The uptake of lead and copper as a function of pH showed that the increase in pH up to 5 resulted in a decrease of the residual lead and copper amounts. This could be explained by the increase in the quantity of the coagulant Al(OH)_3 . If activity—pH diagram for Al (III) species in equilibrium with $\text{Al(OH)}_3(\text{s})$ is investigated, it will be seen that dominant

Al(III) species is in the form of $\text{Al}(\text{OH})_3(\text{s})$ at pH 5.0 - 8.5 interval [19].

Therefore, lead and copper removal by electrocoagulation over 90 % was obtained for an initial pH up to 5.

The removal efficiency of lead and copper peaked at pH of 5 and 6, respectively (Fig. 2). At a neutral pH of 7, both metals demonstrated an optimal and consistent removal efficiency. This value is in agreement with the results obtained by C. Escobar et al [18] who reported that the final pH depends not only on the concentration of metal ions but also the initial pH of the treated water. Several published accounts [20, 21] establish the use of soluble anodes causes a change in the pH of the solution during electrocoagulation.

To investigate this effect, the initial and final pHs of the treated solutions were measured for each electrocoagulation test.

Fig. 3 illustrates the electrolyte pH after electrolysis versus initial pH.

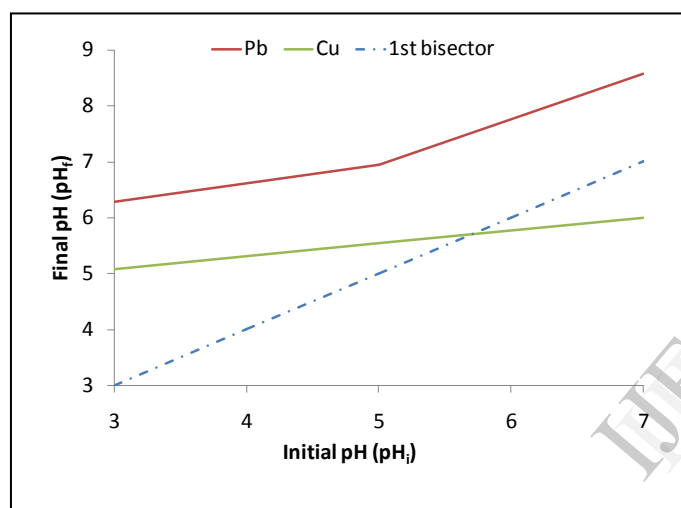


Fig. 3. Evolution of final pH vs. initial pH

As shown, as the initial pH of solution is acidic (3), final pH values rise. The presence of lead ions in the bulk solution results in higher values of electrolyte pH after electrolysis. However, no significant change occurred in the final pH for all bulk solution containing copper ions. At an initial pH upper than 5, OH^- ions can also partially combine with Cu^{2+} to form insoluble copper hydroxide precipitation $\text{Cu}(\text{OH})_2$. An increase in copper removal efficiency was observed (fig. 2). The removal percentage increased up to 99 % for an initial pH value of 7.

In contrast, for an initial pH in the range 5-7, there was a large variation in the final pH for bulk solution containing Pb^{2+} . Regarding this pH variation after electrolysis with aluminum electrodes there is still a certain uncertainty as to its origin. In fact, it could be attributed to hydrogen evolution at the cathode or the transfer of CO_2 [22].

Lead is known to form aqueous complexes with inorganic ligands such as carbonate, chloride, fluoride, nitrate, and sulfate. At pH values exceeding about 6.5, the dominant species are lead-carbonate complexes [23].

When initial pH is about 5, leads ions are almost completely removed by electrocoagulation. This could be explained by mutually adsorption and precipitation phenomena.

Under oxidizing conditions, depending on pH and ligand concentrations, cerussite (PbCO_3), hydrocerussite [$\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$], anglesite (PbSO_4), or chloropyromorphite [$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$] may control aqueous lead concentrations[23].

C. Escobar [18] reported that the pH of the test solution must be considered, since at pH between 0 and 5, the hydroxylated species do not significantly affect metal removal. Other cations were found to behave in a similar manner.

B. Effect of electrolysis time on lead and copper removal

To highlight the effect of the electrolysis time on lead and copper removal, a series of electrocoagulation tests were performed by tracking the concentration of each metal for different electrolysis time spans for an initial pH of 5.

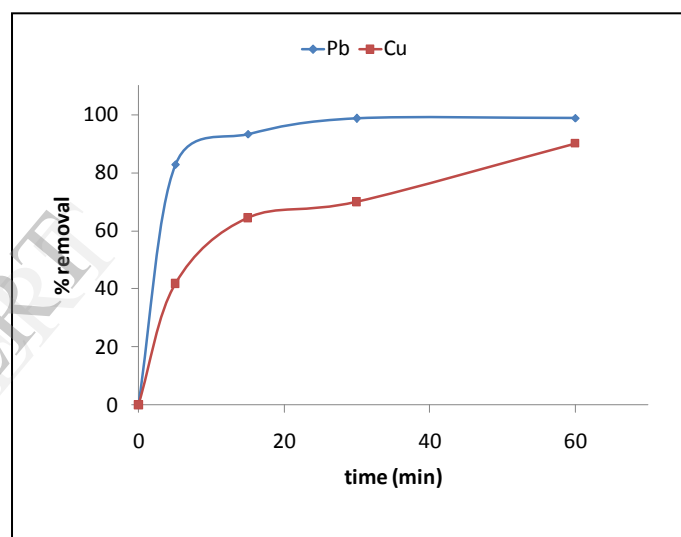


Fig. 4. Variation of lead and copper removal as a function of electrocoagulation time

The study of the effect of electrolysis time on lead and copper removal shows a gradual increase along time, with a maximum removal of 98.7 and 90.2 % respectively occurring in 60 minutes.

According to Fig. 4, metal removal increased significantly during the first stage of electrolysis (15 min). Afterwards, lead removal was not significant. However, copper removal showed a slight increase. Fig. 4 clearly shows that electrocoagulation is more effective for lead removal.

C. Effect of conductivity on lead and copper removal by EC

The addition of electrolyte promotes the electrical transport ensuring better chemical dissolution of aluminum. In these experiments, NaCl was used as background salts. Initial lead and copper concentrations of 70 mg L^{-1} was used. Electrolyses were carried out at $\text{pH} = 5$. During the course of electrolysis, residual metal concentrations were determined. The presence of the chloride ions in solution has been reported

to decrease passivation of the aluminium surface and thereby increase the efficiency of electrocoagulation processes [24].

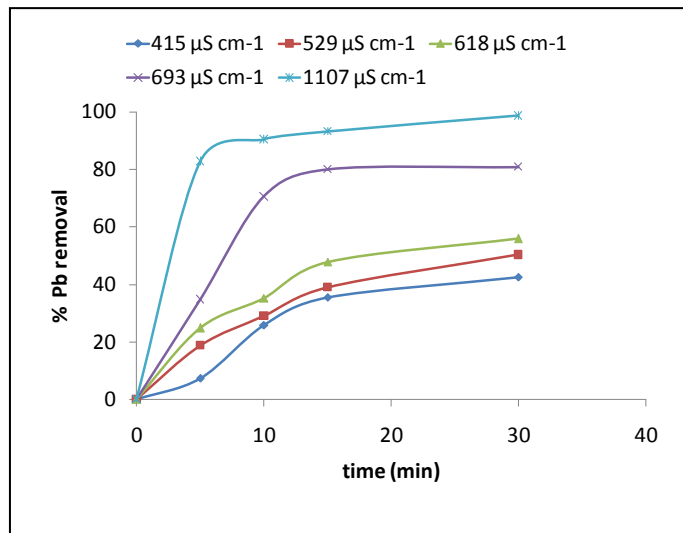


Fig. 5. Evolution of lead removal versus time for different initial conductivities

The effect of initial conductivity on lead and copper removal was examined. From Figure 5, experimental results showed that lead removal increased with increasing initial conductivity. Increasing the initial conductivity from 415 to 1107 $\mu\text{S cm}^{-1}$ resulted in an increase in lead removal efficiency from 42 % to 98 %. For all studied conductivities, appreciable lead removal occurred during the first stage of electrolysis (0 to 15 min) but a slow increase in the final stage.

As shown in Fig. 5, copper ions at different conductivities had almost the same percentage of removal after 30 minutes electrochemical treatment. However, if the percentages of removal with different electrolyte concentrations within a certain treatment time were compared, conductivity was found to have some effects on lead removal speed. With 15 minutes electrochemical treatment, the highest removal was obtained for a conductivity of 1107 $\mu\text{S cm}^{-1}$ and the percentage of copper removal was 64.4 %

The conductivity and the presence of NaCl enhanced the effectiveness of electrocoagulation treatment by virtue of better chemical dissolution.

The electrocoagulation electric energy consumption W (kWh m^{-3}) which is a very important electrocoagulation parameter can be calculated as:

$$W = \frac{U \cdot I \cdot t_{EC}}{V} \quad (2)$$

where U is the applied tension (V), I is the current intensity (A), t_{EC} is the time of EC (s) and V is the volume (m^3) of boron solution.

To highlight the effect of the conductivity on the energy consumption, electrolysis voltage was recorded during each experiment. Table 1. depicts the effect of conductivity on electrolysis voltage and energy consumption.

As conductivity increases, the cell voltage decreases. The decrease of electrolysis potential difference can be related to

ohmic potential drop of the solution and/or to a decrease of the anode overpotential [22].

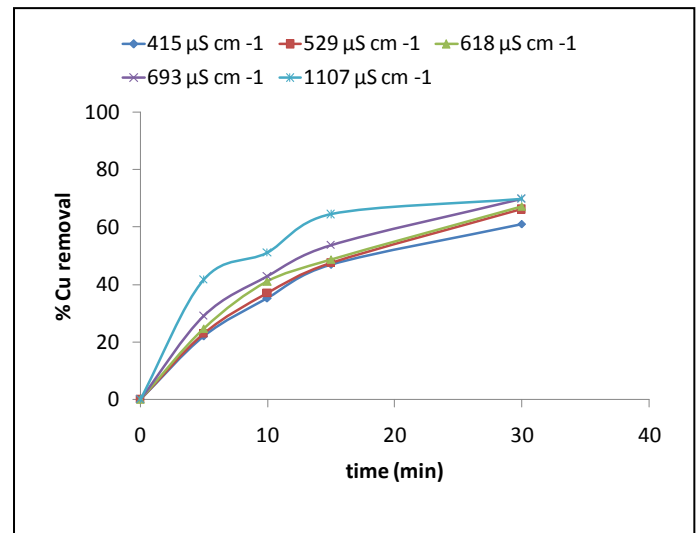


Fig. 6. Evolution of copper removal versus time for different initial conductivities

TABLE I. VARIATION OF ELECTROLYSIS VOLTAGE AND ENERGY CONSUMPTION AS A FUNCTION OF INITIAL CONDUCTIVITY.

Conductivity ($\mu\text{S cm}^{-1}$)	415	529	618	693	1107
U (V)	7.7	6.7	5.9	5.3	3.5
Pb					
W (kWh m^{-3})	0.481	0.418	0.369	0.331	0.219
Cu					
U (V)	6.0	5.5	4.6	4.1	3.3
W (kWh m^{-3})	0.375	0.344	0.288	0.256	0.206

Thus, energy consumption decreases by increasing initial conductivity. A higher conductivity results in better removal efficiency and lower energy consumption.

D. Effect of current density

In all electrochemical process, the current density is the most important parameter for controlling the reaction rate within the electrochemical reactor [25]. When the current density increased, the processing time decreased due to the strong dissolution of the electrodes. This resulted in further destabilization of pollutants as well as an increase in the production rate of hydrogen bubbles whose size decreased as the current density increased [26]. To investigate the effect of current density, a series of EC experiments were carried out at $\text{pH} = 5$ for current intensities ranging from 0.01 to 0.1 V. Fig. 7. shows the effect of applied current density on electrocoagulation efficiency. It can be noticed that the rate of percentage lead and copper removal increases with an increase in current density.

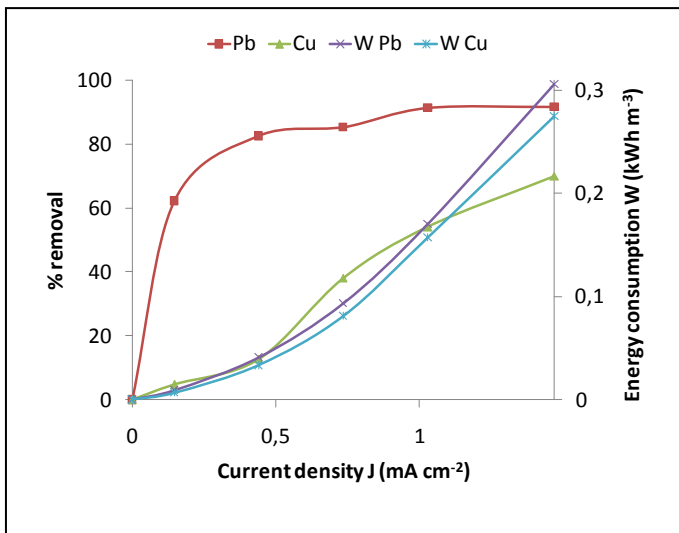


Fig. 7. Variation of lead and copper removal and energy consumption as a function of current density

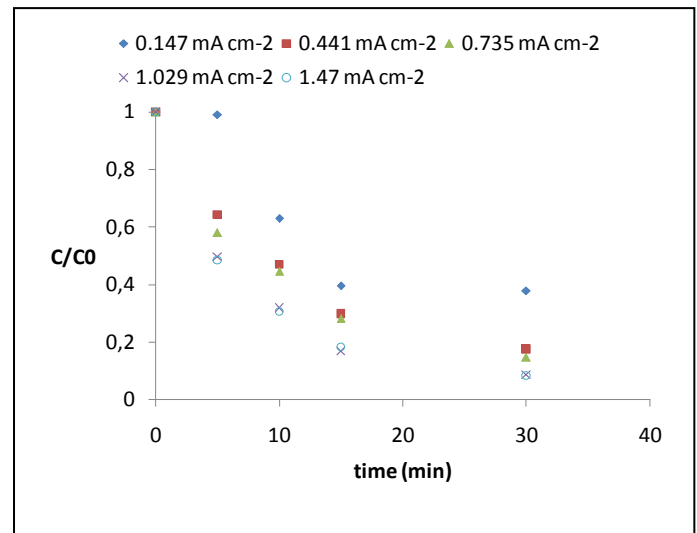


Fig. 9. Effect of the current density on the removal of lead by electrocoagulation process

The trend of percentage removal with current density is not similar for both studied metals ions in this work. From Fig. 7, it was well seen that the uptake of lead increased with increase in current density and remained nearly constant.

After 30 minute the amount of lead removed increased from 62 to 83 % as the current density increased from 0.147 to 0.441 mA cm⁻². Whereas, experiments on copper removal under different applied current densities revealed that removal efficiency was of less significance as current density was below 0.441 mA cm⁻². This can be explained that at lower current densities the amount of flocs generation is less.

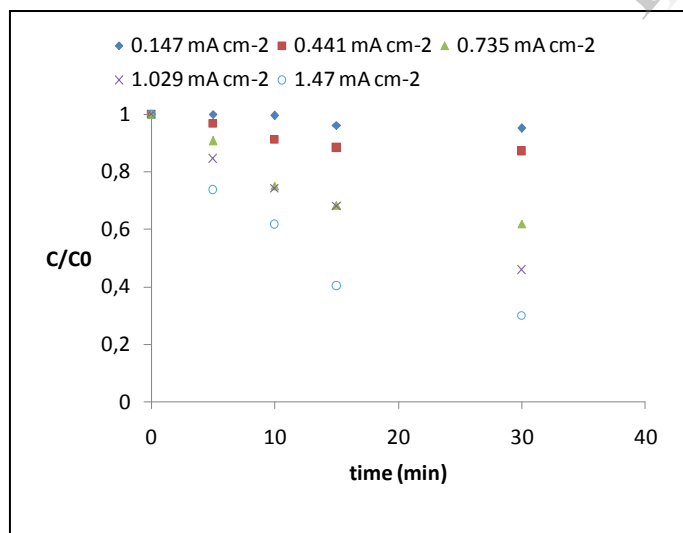


Fig. 8. Effect of the current density on the removal of copper by electrocoagulation process

Fig. 8 and Fig. 9 depict that the rate of percentage removal is high in the beginning of the process and is almost slow at later stage of the process.

It can also be observed that when the current density increased, the operating time decreased. This could be attributed to the increase of the amount of Al³⁺ released. However, the difference between the curves corresponding to different current density became small when it was higher than 0.735 mA cm⁻².

It was found that the increase in current density was accompanied by an increase in the difference of potential between the two electrodes, which led to an increase in energy consumption (Fig. 7). In addition to that, a high current density on the one hand caused a reduction of cathode passivation and, on the other hand, led to a high level of energy consumption by Joule effect. It would be more efficient to work at low current densities [27]. However, long reaction time was undesirable from the engineering viewpoint. Conciliation must be found between economically suitable energy and removal efficiency.

For this reason, a current density of 1.029 appeared to be optimal in terms of energy consumption, in terms of preventing the rapid dissolution of the electrodes and in terms of removal. The lead and copper reached a value of 91.4 and 54.1 % respectively.

IV. CONCLUSION

The aim of this study was to highlight the effect of some parameters on the efficiency of electrocoagulation process such as initial pH, current density, conductivity, and operating time. It was found that electrocoagulation is more effective for lead removal. Results showed that optimum removal efficiencies were achieved at a current density of 1.029 mA cm⁻² and pH of 5. Both lead and copper removal was found rapid at higher current densities. Lead was observed to be better removed from aqueous solution for higher initial conductivity current densities. The removal mechanisms seem to be distinct when considering lead and copper. Although it is a first step to improve the knowledge regarding lead and

copper removal by electrocoagulation with aluminum electrodes, this work generated important information on the optimal conditions of several variables that influence electrocoagulation.

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