

Treatment of electroplating wastewater containing Cu^{2+} , Zn^{2+} and Cr(VI) by electrocoagulation

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Abstract

The performance of electrocoagulation, with aluminium sacrificial anode, in the treatment of metal ions (Cu^{2+} , Zn^{2+} and Cr(VI)) containing wastewater, has been investigated. Several working parameters, such as pH, current density and metal ion concentrations were studied in an attempt to achieve a higher removal capacity. Results obtained with synthetic wastewater revealed that the most effective removal capacities of studied metals could be achieved when the pH was kept between 4 and 8. In addition, the increase of current density, in the range 0.8–4.8 A dm⁻², enhanced the treatment rate without affecting the charge loading, required to reduce metal ion concentrations under the admissible legal levels. The removal rates of copper and zinc were found to be five times quicker than chromium because of a difference in the removal mechanisms. The process was successfully applied to the treatment of an electroplating wastewater where an effective reduction of (Cu^{2+} , Zn^{2+} and Cr(VI)) concentrations under legal limits was obtained, just after 20 min. The electrode and electricity consumptions were found to be 1 g l⁻¹ and 32 A h l⁻¹, respectively. The method was found to be highly efficient and relatively fast compared to conventional existing techniques.

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1. Introduction

Effluents issued from surface finishing and plating industry usually contain, metal-ion concentrations much higher than the permissible levels. Due to their high toxicity, industrial wastewaters containing heavy metals are strictly regulated and must be treated before being discharged in the environment. Various techniques have been employed for the treatment of heavy metals, including precipitation, adsorption, ion-exchange and reverse osmosis. Precipitation is most applicable among these techniques and considered to be the most economical [1]. It is based on chemical coagulation by adding lime to raise the pH and aluminium salt to remove colloidal matter as gelatinous hydroxides. Activated silica or polyelectrolytes may also be added to stimulate coagulation. The former treatment may be followed by adsorption onto activated carbon to complete metals removal

at the ppm level [2]. Although, it is shown to be quite effective in treating industrial effluents, the chemical coagulation may induce secondary pollution caused by added chemical substances. This drawback, together with the need for low cost effective treatment, encouraged many studies on the use of electrocoagulation for the treatment of several industrial effluents.

Electrocoagulation is a simple and efficient method where the flocculating agent is generated by electro-oxidation of a sacrificial anode, generally made of iron or aluminium. In this process, the treatment is done without adding any chemical coagulant or flocculant, thus reducing the amount of sludge which must be disposed [3]. The electrocoagulation has been successfully used to treat oil wastes, with a removal efficiencies as high as 99% [4,5]. A similar success was obtained when treating dye-containing solutions [6–8], potable water [9], urban and restaurant wastewater [10,11] and nitrate or fluoride containing waters [12,13]. In addition, a great deal of work performed in the last decades [14–17] has proved that electrocoagulation is an effective technology for the treatment of heavy metal containing solutions.

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In the present work, the efficiency of electrocoagulation in removing copper, zinc and chromium from wastewater of an electroplating unit was reported. The effect of the wastewater characteristics, initial pH and metal-ion concentrations and operational variables, current density and treatment time, on the removal efficiency is explored and discussed to determine the optimum operational conditions. The optimum operational parameters were used for wastewater treatment of a local electroplating unit.

2. Experimental details

2.1. Reagents

The electrodes used in this study consisted of aluminium plates (100 mm × 50 mm × 0.5 mm) of 99% purity, purchased from Prolabo, France. All other chemicals were of analytical grade and supplied by Fluka, France. Stock synthetic wastewater solutions of 800 mg l⁻¹ chromium, copper or zinc were, respectively, prepared by dissolving the required amounts of potassium dichromate, copper sulphate or zinc sulphate in water. Solutions of lower concentrations were prepared by proper dilution.

The pH of the solution was adjusted to the required value with 10⁻² M hydrochloric acid and 10⁻² M sodium hydroxide.

All measurements were carried out at ambient temperature (25 ± 1 °C), on 200 ml aliquots of synthetic or real industrial wastewater (collected from an electroplating unit) added with the same amount of potassium chloride (0.74 g) to avoid excessive ohmic drop and to limit the formation of the passivation layer on aluminium electrodes. As has been shown in previous study [18], the addition of halide salts will decrease the energy consumption and limit the temperature variations, due to the Joule effect.

2.2. Electrocoagulation procedure

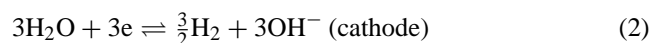
Electrocoagulation was carried out in a 250 ml beaker without stirring, using three parallel aluminium electrodes spaced by 5 mm and dipped in the wastewater. A radiometer potentiostat/galvanostat of the type DEA 332 interfaced to an IBM personal computer was used in galvanostatic mode to supply a constant current. The electrodes were connected in such a manner that the central electrode functioned as a sacrificial anode (active surface = 50 cm²), while the two others operated as cathodes.

To follow the progress of the treatment, samples of 2 ml were periodically taken from the reactor then filtered to eliminate sludge formed during electrolysis. The residual concentrations of metal ions were determined by atomic absorption spectrophotometer (Perkin–Elmer, model Analyst 300). At the end of the experiment, the solution was filtered and the precipitate was dried and weighed.

When a real industrial wastewater was treated, the decrease of chemical oxygen demand (COD) was measured, using a COD reactor and direct reading spectrophotometer (Beckman model DU 530).

3. Brief description of electrocoagulation mechanism

Electrocoagulation is based on the in situ formation of the coagulant as the sacrificial anode corrodes due to an applied current, while the simultaneous evolution of hydrogen at the cathode allows for pollutant removal by flotation. This technique combine three main interdependent process, operating synergistically to remove pollutants: electrochemistry, coagulation and hydrodynamics. An examination of the chemical reactions occurring in the electrocoagulation process shows that the main reactions occurring at the electrodes are:



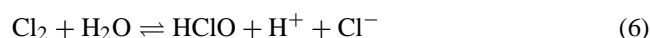
In addition, Al³⁺ and OH⁻ ions generated at electrode surfaces react in the bulk wastewater to form aluminium hydroxide:



If the anode potential is sufficiently high, secondary reactions may occur at the anode, such as direct oxidation of organic compounds and of H₂O or Cl⁻ present in wastewater:



The produced chlorine undergoes a dismutation reaction at pH higher than 3–4:



The aluminium hydroxide flocs act as adsorbents and/or traps for metal ions and so eliminate them from the solution. Furthermore, a direct electrochemical reduction of Cr(VI) in Cr(III) may occurs at the cathode surface [3,16,19]. Simultaneously, the hydroxyl ions which are produced at the cathode, increase the pH in the electrolyte and may induce coprecipitation of Cu²⁺, Zn²⁺ and Cr(III) in the form of their corresponding hydroxides [3,4,9]. This acts synergistically to remove pollutants from water.

4. Results and discussion

The electrocoagulation process is quite complex and may be affected by several operating parameters, such as pollutants concentrations, initial pH and current density. In order to enhance the process performance, the effects of those parameters have been explored.

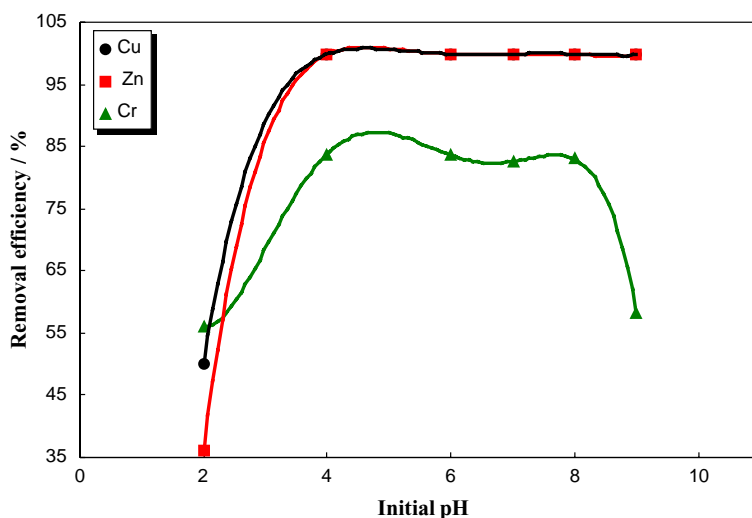


Fig. 1. Effect of initial pH on metal ions removal. Initial concentrations of Cu^{2+} , Zn^{2+} and Cr(VI) = 50 mg l^{-1} each, $j = 1.6 \text{ A dm}^{-2}$, anode surface = 50 cm^2 , time of electrolysis = 20 min.

4.1. Effect of initial pH

It has been established that the initial pH [8,11] has a considerable influence on the performance of electrocoagulation process. To evaluate its effect, a series of experiments were performed, using solutions containing a mixture of Cu^{2+} , Zn^{2+} and Cr(VI) of 50 mg l^{-1} each, with an initial pH varying in the range 2–10.

As illustrated in Fig. 1, the removal efficiencies (R_e) of copper and zinc, after 15 min of electrolysis at 0.8 A, reached value as high as 99.9%, when pH exceed 4. In the same conditions, the removal yield of chromium reached a maximum of about 83% and seemed to be not affected by pH, as long as this later is kept in the range between 4 and 8. In contrast, when the initial pH is increased above 8, a dramatic decrease of the removal efficiency of chromium is

observed (58%), while removal yields of Cu^{2+} and Zn^{2+} remained very high. Furthermore, it can be seen that the removal efficiency of all studied ions decreased significantly upon decreasing initial pH. Removal yield lower than 55% was achieved at pH 2. The decrease of R_e at a pH less than 4 and higher than 8 was observed by many investigators and was attributed to an amphoteric behaviour of Al(OH)_3 which lead to soluble Al^{3+} cations, when the initial pH is low and to monomeric anions Al(OH)_4^- , when the initial pH is high [8]. These soluble species are useless for water treatment. When the initial pH was kept in the range 4–8, all aluminium cations produced at the anode formed polymeric species $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ [20,21] and precipitated Al(OH)_3 leading to a more effective treatment. The high efficiency of Cu and Zn removal, even at a high pH, might be ascribed to the precipitation of their hydroxides at the cathode, which

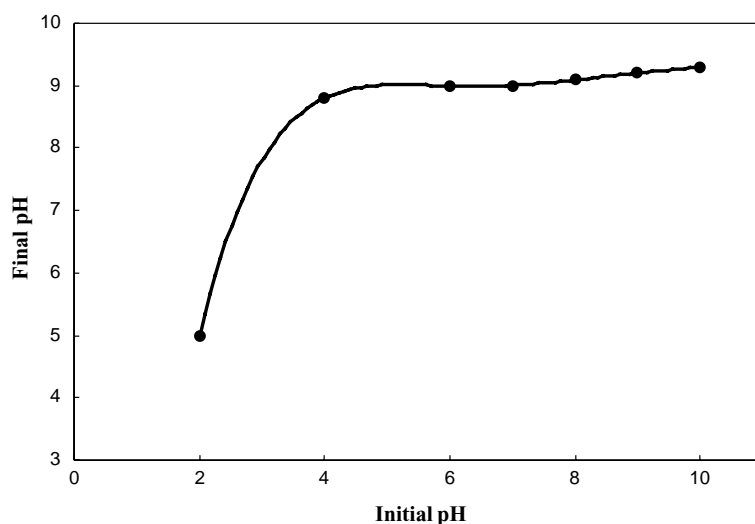


Fig. 2. pH variation after electrocoagulation. Initial concentrations of Cu^{2+} , Zn^{2+} and Cr(VI) = 50 mg l^{-1} each, $j = 1.6 \text{ A dm}^{-2}$, anode surface = 50 cm^2 , time of electrolysis = 40 min.

start at pH ~ 6 –7 for copper and ~ 7 –8 for zinc. At alkaline pH between 8 and 10, dichromate ions are converted to soluble chromate (CrO_4^{2-}) anions, which goes some way towards explaining its less effective removal.

As observed by other investigators [9,11], the treatment induced an increase in the pH when the initial pH was low (between 2 and 9) as shown in Fig. 2. This might be explained by the excess of hydroxyl ions produced at the cathode in sufficiently acidic conditions and by the liberation of OH^- due to the occurrence of a partial exchange of Cl^- with OH^- in $\text{Al}(\text{OH})_3$ [11]. When the initial pH is above 9, the formation of $\text{Al}(\text{OH})_4^-$ species together with parasite attack of the cathode by hydroxyl ions [18] lead to a slight decrease in the pH.

As a result of the previous discussion of the effect of pH on the removal efficiency, the initial pH was adjusted to 6 for all subsequent studies.

4.2. The effect of current density

The current density not only determines the coagulant dosage rate, but also the bubble production rate and size [21,22]. Thus, this parameter should have a significant impact on pollutants removal efficiencies.

To investigate the effect of current density and charge loading on the removal yield, a series of experiments were carried out on solutions containing a constant pollutants loading with current density being varied from 0.8 to 4.8 A dm^{-2} . Fig. 3 is a semi-logarithmic plot, showing the normalised concentrations profiles of the studied metal ions for typical electrocoagulation runs, where the initial pH was fixed at 6. The removal rate of all studied metal ions increased upon increasing current density. The highest current (4.8 A dm^{-2}) produced the quickest removal rate, with a 96% concentration reduction occurring just after 10 min. This expected behaviour is easily explained by the increase of coagulant and bubbles generation rate, resulting in a more efficient and faster removal, when the current is increased [21,23]. Indeed, the amounts of aluminium and hydroxide ions generated at a given time, within the electrocoagulation cell are related to the current flow, using Faraday's law:

$$m = \frac{ItM}{zF} \quad (8)$$

where I is the current intensity, t is the time, M is the molecular weight of aluminium or hydroxide ion (g mol^{-1}), z is the number of electrons transferred in the reaction (3 for aluminium and 1 for hydroxide) and F is the Faraday's constant (96486 C mol^{-1}).

Moreover, it was previously shown that the bubble size decreases with increasing current density [22], which is beneficial to the separation process. Nevertheless, as the time progresses, the amount of oxidised aluminium and the required charge loading increase. However, these parameters should be kept at low level to achieve a low-cost treatment.

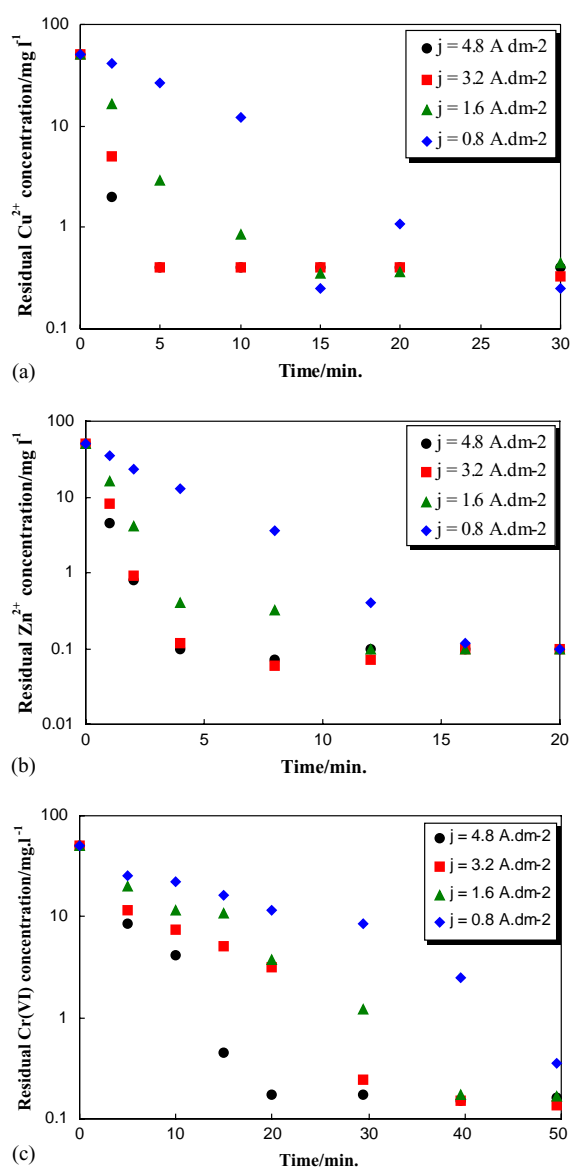


Fig. 3. Effect of current density on the removal rate of Cu^{2+} (a), Zn^{2+} (b) and $\text{Cr}(\text{VI})$ (c) initial concentrations of Cu^{2+} , Zn^{2+} and $\text{Cr}(\text{VI}) = 50 \text{ mg l}^{-1}$ each, anode surface = 50 cm^2 .

To optimise the treatment efficiency, optimum charge loading required to achieve high removal yields (residual concentration under 2 mg l^{-1}) for each metal ion, were calculated at different current densities. The results shown in Fig. 4, pointed out that the removal rate of zinc is almost two times faster than that of copper and five times faster than chromium. Indeed, the volumetric electrical charges ensuring 96% removal of zinc and copper were, respectively, 9 and 17.4 mF l^{-1} , while that needed to achieve the same removal efficiency of chromium was 59.4 mF l^{-1} . Furthermore, as observed by other investigators [21,23], a slight increase of charge loading is observed for chromium, when current density was varied in the range 0.8 – 4.8 A dm^{-2} . At high current, the bubble density and upwards flux increased

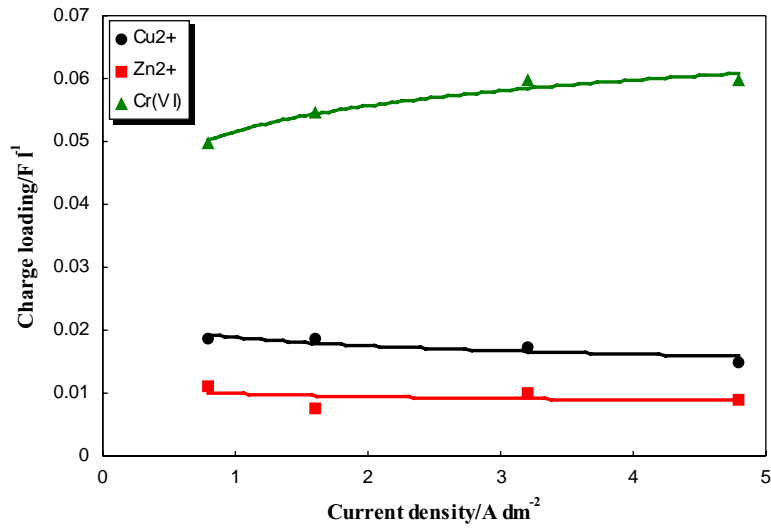


Fig. 4. The effect of current density on charge loading. Initial concentrations of Cu²⁺, Zn²⁺ and Cr(VI) = 50 mg l⁻¹ each, anode surface = 50 cm².

and resulted in a faster removal of the coagulant by flotation. Hence, there is a reduction in the probability of collision between the coagulant and pollutants. Nevertheless, when Cu²⁺ or Zn²⁺ are considered, the required charge loading are not affected by current. The differences of behaviour and removal rates between Cu²⁺, Zn²⁺ and Cr(VI) could be attributed to a difference in the removal mechanisms. Indeed, coprecipitation of Cu(OH)₂ and Zn(OH)₂ may play a dominant role in the removal mechanism of the corresponding metallic ions. Regardless the slight increase (below 20%) of the charge loading observed for Cr(VI), the time required to achieve the removal can be shortened by a factor of six, when current density is increased from 0.8 to 4.8 A dm⁻², while the cost of the treatment remained unchanged. Hence, the highest current should be selected to obtain the quickest removal rate.

4.3. The effect of metal ion concentration

In order to examine the effect of metal ion concentration present in the wastewater on the removal rate, several solutions containing increased concentrations (50–800 mg l⁻¹) of Cu²⁺, Zn²⁺ and Cr(VI) were treated and the residual concentrations of ions were measured at different times of electrolysis.

Fig. 5 shows the change in the removal rate of zinc with initial concentration. Copper and chromium removal rates showed the same trends. As expected, it appears that the removal rate has decreased upon increasing initial concentration. This induced a significant increase of charge loading required to reach residual metal concentrations below the levels admissible for effluents discharged into the sewage system (2 mg l⁻¹), as shown in Fig. 6. It can be observed that

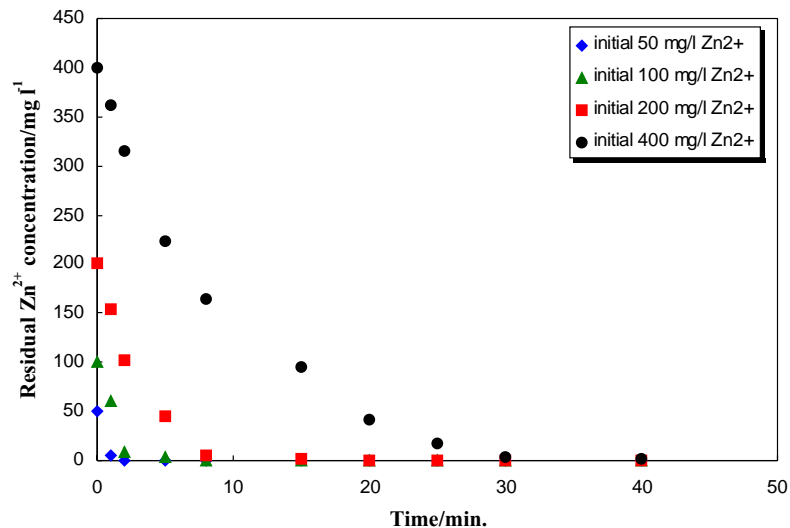


Fig. 5. The effect of initial concentration on the removal efficiency of zinc ions. $j = 4.8 \text{ A dm}^{-2}$, anode surface = 50 cm².

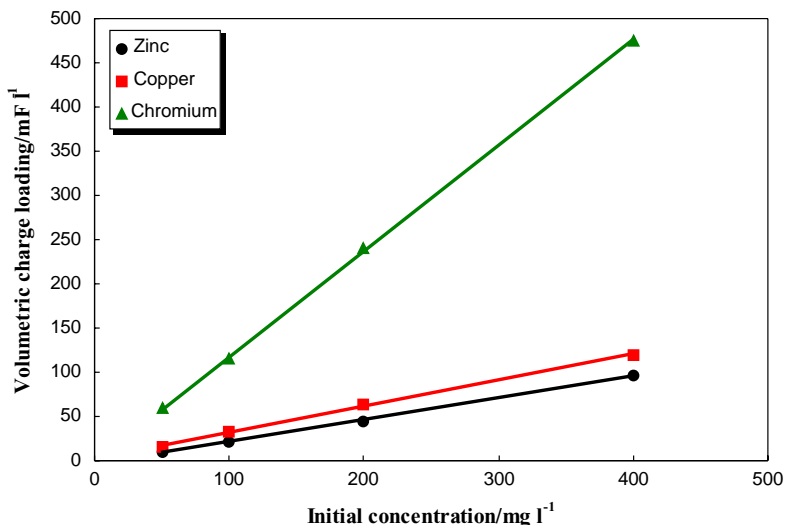


Fig. 6. The effect of initial concentration on the charge loadings required for an effective removal of Zn^{2+} , Cu^{2+} and $Cr(VI)$ $j = 4.8 \text{ A dm}^{-2}$, anode surface = 50 cm^2 .

charge loading undergo a linear increase with initial concentration. This result proves that the amount of aluminium delivered per unit of pollutants removed is not affected by the initial concentration. In addition, the charge loading required to remove chromium to the admissible level, is much higher than that required for Cu^{2+} and Zn^{2+} . This confirmed the less efficient removal of chromium compared to copper and zinc and indicated that longer electrolysis time is necessary for chromium removal. Indeed, at high initial concentration (200 mg l^{-1}), zinc and copper were reduced to admissible levels after only 15 min. However, 1 h was necessary to achieve the efficient removal of chromium.

4.4. Treatment of an industrial wastewater

To validate the suitability of electrocoagulation for the treatment of industrial wastewater, an electrolysis was car-

ried, using a wastewater sample, collected from an electroplating unit and the residual concentrations of Cu^{2+} , Zn^{2+} and $Cr(VI)$ together with COD were measured at different times of electrolysis.

The initial concentrations of Cu (33 mg l^{-1}), Zn (41 mg l^{-1}) and Cr (24 mg l^{-1}) were shown to exceed the prescribed legal limits. In addition, the COD content of the wastewater (302 mg l^{-1}) was found to be more than two times the authorised limit, indicating the presence of some organic compounds which were added to the electroplating bath as brighteners, levellers or wetting agents.

It appears from the results shown in Fig. 7 that the residual concentrations of copper and zinc were rapidly reduced under the legal limits, just after 5 min. Whereas, the residual concentration of chromium decreased more slowly and reached 2 mg l^{-1} after an electrolysis time of 20 min. The removal rates of metal ions seems to be relatively slow

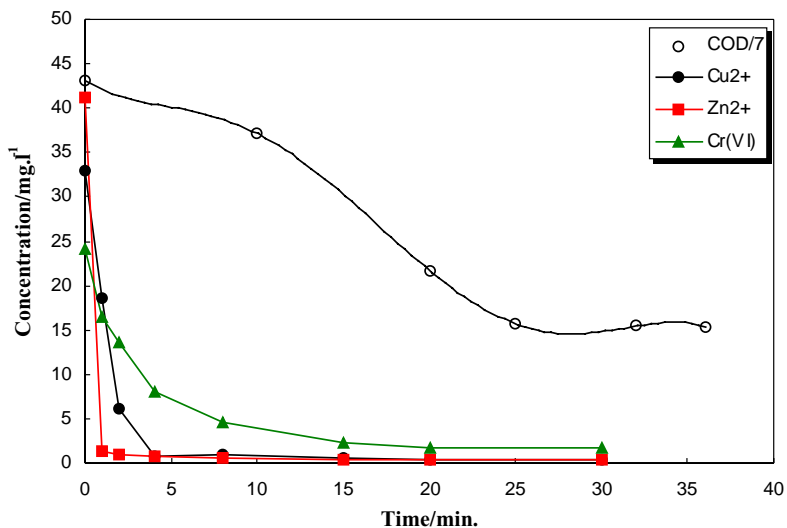


Fig. 7. Effect of electrolysis time on the residual concentrations and COD content. $j = 4.8 \text{ A dm}^{-2}$, anode surface = 50 cm^2 .

compared to the removal from synthetic wastewater. This, probably, resulted from the presence of organic compounds which may competitively adsorb on $\text{Al}(\text{OH})_3$ coagulant, leading to a substantial reduction of metal ions removal.

The measured COD decreased from 302 mg l^{-1} to less than 110 mg l^{-1} after 25 min., which corresponds to a removal efficiency of about 64%. Beyond that time, the residual COD reached a plateau and remained nearly constant. The electrode and volumetric electricity consumptions needed to achieve an effective treatment of the studied industrial wastewater were found to be 1 g l^{-1} and 32 A h l^{-1} , respectively.

All these results give an indisputable evidence that electrocoagulation can effectively reduce metal ions to a very low level. Dissolved organic compounds present in electroplating unit wastewater are also removed. Consequently, electrocoagulation could be an efficient method for heavy metal removal from industrial wastewater.

5. Conclusion

The results of this study have shown the applicability of electrocoagulation in the treatment of electroplating wastewater containing copper, zinc and chromium. The most effective removal capacity was achieved in the pH range between 4 and 8. The treatment rate was shown to increase upon increasing the current density. Indeed, the highest current produced the quickest treatment with an effective reduction of Cu and Zn concentrations in the industrial wastewater under the admissible level, after only 5 min. Whereas, 20 min. were needed to achieve an equivalent removal of Cr(VI). The slower removal of chromium compared to copper and zinc is attributed to a difference in the removal mechanisms. Moreover, the charge loading required to achieve an effective treatment, increased with initial concentration. In comparison to chemical coagulation [24], where several hours are needed and adsorption on activated carbon [25], the electrocoagulation method achieves faster removal of pollutants.

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