Effect of anions on removing Cu²⁺, Mn²⁺ and Zn²⁺ in electrocoagulation process using aluminum electrodes

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ABSTRACT

In the present study, the performance of electrocoagulation process with aluminum electrodes in the treatment of Cu^{2+}, Zn^{2+} and Mn^{2+} containing aqueous solutions was investigated by depending on type of anion in solution, considering some operating conditions such as initial metal concentration and pH. Results obtained from synthetic wastewater showed that type of anion in solutions has a significant effect on the metal removal. The initial concentration of zinc influenced significantly the performance of electrocoagulation process as compared with the results obtained from Mn and Cu metals. Anions studied did not generate an important difference between pH variations. Best removals for three metals were achieved with increasing the pH in the presence of both anions. Total removals of copper and zinc reached almost 100% after 5 min at pH values > 7. At the end of the experiments for 35 min, the Mn removals were 85 and 80% in the presence of sulfate and chloride anions, respectively.

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1. Introduction

A number of the industrial effluents contain toxic metals such as Cd, Cr, Cu, Ni and Zn, which are harmful to the environment when they are directly discharged. They can be easily absorbed by fishes and vegetables due to their high solubility in the aquatic environments. Hence they may accumulate in the human body by means of the food chain [1–3]. To eliminate their adverse effects on human and ecology, it is absolutely necessary to treat wastewater including these metals before being discharged. Up to now, several techniques such as chemical precipitation, coagulation–flocculation, flotation, ion exchange, membrane separation, solvent extraction, adsorption and electrocoagulation (EC) have been applied to remove heavy metals from industrial effluents [1]. Among the various techniques mentioned above, electrocoagulation has been found to be quite interesting both for economical and environmental reasons [4]. EC has been successfully applied to remove soluble ionic species from solutions, particularly heavy metals [3,5].

Electrocoagulation (EC) 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. In the electrocoagulation process, main reactions occurring at the electrodes are:

$$Al \leftrightarrow Al^{3+} + 3e^{-} \quad \text{(anode)} \tag{1}$$

$$3H_2O + 3e^{-} \leftrightarrow (3/2)H_2 + 3OH^{-} \quad \text{(cathode)} \tag{2}$$

In addition, Al^{3+} and OH^{-} ions generated at electrode surfaces react in the bulk wastewater to form aluminum hydroxide:

$$Al^{3+} + 3OH^{-} \leftrightarrow Al(OH)_3 \tag{3}$$

The aluminum hydroxide flocs act as adsorbents and/or traps for metal ions and so eliminate them from the solution. Simultaneously, the hydroxyl ions produced at the cathode increase the pH in the electrolyte and may induce coprecipitation of metals in the form of their hydroxides [5–7]. It has been reported that the initial pH has a considerable influence on the performance of electrocoagulation process [3,5,8]. In addition, chemical dissolution of aluminum is strongly influenced by the pH [9].

Many studies on the effects of various parameters such as pH, initial concentration, current density, inter-electrode distance and conductivity have been performed; there is a little knowledge about the anion effect on metal removal due to limited studies in the literature [10–14]. In this study, the effect of anions on removing Cu, Zn and Mn by electrocoagulation was investigated on solutions containing the sulfate and chloride at different operating parameters such as initial concentration, operating time and initial pH.

2. Materials and methods

Stock solutions of 1000 mg/L Cu, Zn and Mn were prepared with sulfate and chloride salts of each metal. Experiments were performed in two stages. In the first stage, to examine the effect of initial metal concentrations on the system performance, six

Table 1
Characteristics of the experiments.

The code of runs	The conditions of runs	The code of runs	The conditions of runs	The code of runs	The conditions of runs
CS1	Cu = 50 mg/L SO_4^{2-} = 75.6 mg/L	ZS1	Zn = 50 mg/L SO_4^{2-} = 73.4 mg/L	MS1	Mn = 50 mg/L SO_4^{2-} = 87.4 mg/L
CS2	Cu = 100 mg/L SO_4^{2-} = 151.2 mg/L	ZS2	Zn = 100 mg/L SO_4^{2-} = 146.8 mg/L	MS2	Mn = 100 mg/L SO_4^{2-} = 174.8 mg/L
CS3	Cu = 200 mg/L SO_4^{2-} = 302.4 mg/L	ZS3	Zn = 200 mg/L SO_4^{2-} = 293.6 mg/L	MS3	Mn = 200 mg/L SO_4^{2-} = 349.7 mg/L
CC1	Cu = 50 mg/L Cl^- = 56 mg/L	ZC1	Zn = 50 mg/L Cl^- = 54.4 mg/L	MC1	Mn = 50 mg/L Cl^- = 64.8 mg/L
CC2	Cu = 100 mg/L Cl^- = 112 mg/L	ZC2	Zn = 100 mg/L Cl^- = 108.8 mg/L	MC2	Mn = 100 mg/L Cl^- = 129.6 mg/L
CC3	Cu = 200 mg/L Cl^- = 224 mg/L	ZC3	Zn = 200 mg/L Cl^- = 217.6 mg/L	MC3	Mn = 200 mg/L Cl^- = 259.2 mg/L

solutions, which were prepared individually from $CuSO_4·5H_2O$, $MnSO_4·H_2O$, $ZnSO_4·7H_2O$, $CuCl_2$, $MnCl_2·4H_2O$ and $ZnCl_2$, were used in the EC setup at different concentrations (50–200 mg/L) and a constant pH value (pH = 3). The pH increased over time during operation. In the second stage, the influence of pH was examined to ensure a better elimination of metal ions. The experiments were conducted with initial pH varying in the range of 4–9 at initial metal concentrations of 200 mg/L.

Experiments were made by using 750-mL beakers on magnetic stirrers. Four aluminum electrodes (80 mm × 40 mm × 2 mm) were installed vertically with a spacer to ensure fixed distance of 5 mm. The electrodes with total active area of 128 cm^2 were operated in monopolar mode. The electrode surfaces were rinsed with diluted HNO_3 and deionized water and then dried to eliminate the oxides and passivation layers. A DC-power supply was used to apply a current density of 15 mA/cm^2.

To determine the system performance, samples of 7.5 mL were periodically taken from the reactor at intervals of 5 min and then filtered to eliminate sludge formed during electrolysis. The residual concentrations of metal ions were determined by an atomic absorption spectrophotometer (UNICAM 929). The pH was monitored with a pH-meter (Hache Lange HQ40D). The experimental procedure has been given in Table 1.

3. Results and discussion

3.1. Effect of metal concentration

The pH varied over time due to the oxidation/reduction reactions at the anode and cathode during the process. The most probable species that are responsible for electrocoagulation efficiency in the pH range 5–9.5 are polymeric hydroxoaluminum ions and the $Al(OH)_3$ aluminum hydroxide precipitate [15]. Several processes such as metal deposition on cathode, precipitation and co-precipitation of metals and more importantly high sorption capacity of polymeric aluminum hydroxides generated by anodic dissolution resulted in high removal of metals [16,17]. Fig. 1 indicates the variations of pH and copper concentration in the bulk solutions. The results of Cu removal indicated that the effect of anions in the solutions was more considerable rather than initial concentration. While the profiles of Cu (II) removal in the presence of sulfate increased rapidly and reached 75% after 5 min, it increased slowly in the presence of chloride and occurred to be 49% at 5 min in CC3. As shown in Fig. 1(A), the pH is behaved increasingly as similar to that in CS2. The pH change in the case of CS1 was slower relatively than those in the case of CS2 and CS3. The pH change in the presence of chloride was distinctly monitored in CC3, which Cu (II) and Cl^- concentrations in the bulk solution were, respectively, 200 and 224 mg/L, as seen in Fig. 1(B). There was no considerable difference in pH variations at the lower concentrations of cation and anion, both the experiments of CC1 and CC2.

In contrast to the results obtained from copper removal, the zinc removal was significantly based on the initial concentration in existence of chloride ions as shown in Fig. 2. The residual Zn concentration decreased linearly with decreasing the initial concentration at the end of the experiments conducted with chloride anions. A similar behavior was reported by Adhoum et al. [5], during the treatment of metal solutions by electrocoagulation. For instance, the removal efficiencies of Zn were calculated to be 94 and 48% at the end of the ZS1 and ZS2, respectively. This indicated that the removal efficiency decreased with an increase in the Zn concentration. As similar, Merzouk et al. [8] reported that the removal efficiency decreased from 99 to 70% while increasing the metal concentration from 50 to 600 mg/L. The pH variation in the experi-
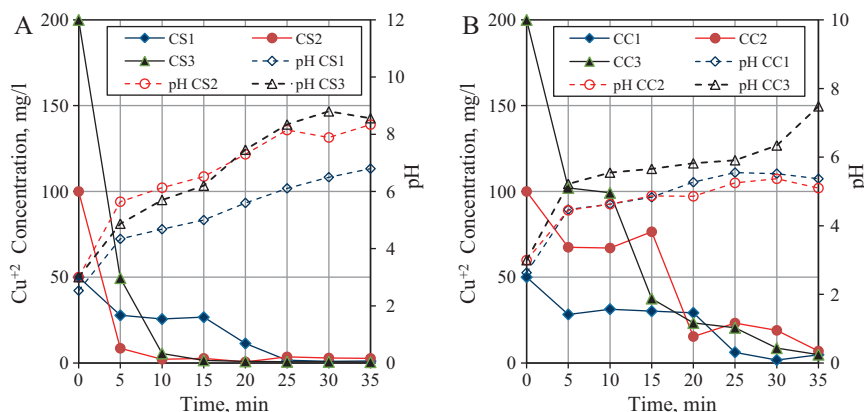
Fig. 1. Changes in copper concentration and pH in the presence of (A) sulfate and (B) chloride as a function of initial concentration.
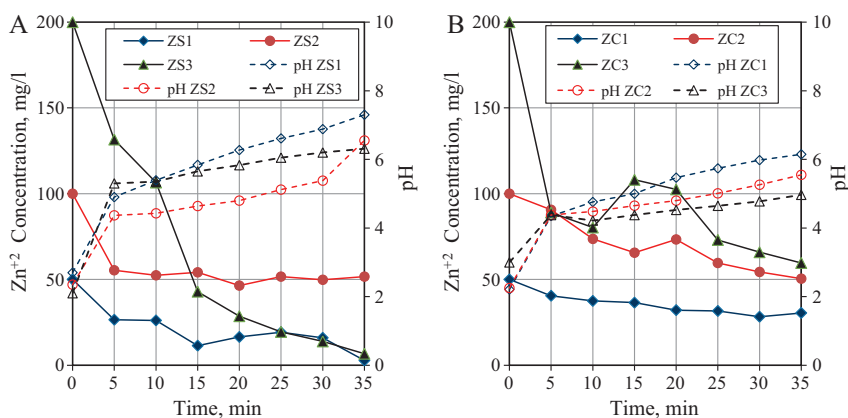
Fig. 2. Changes in zinc concentration and pH in the presence of (A) sulfate and (B) chloride as a function of initial concentration.

ments carried out for Zn removal was partially different from those at the experimental carried out for Cu. The results showed that the highest increases in pH were in ZS1 (Zn and SO_4^{2-} concentrations were 50 and 73.4 mg/L, respectively) and ZC1 (Zn and Cl^- concentrations were 50 and 54.4 mg/L, respectively). At the end of the runs, the pH was 6.15 and 7.3 in the ZC1 and ZS1, respectively. It was found that increasing the initial Zn concentrations from 50 to 200 mg/L resulted in lower pH values during electrocoagulation process. As mentioned above, the results obtained from all the experiments in the presence of sulfate ions were more considerable than those in the presence of chloride ions in terms of removing metals.

Fig. 3 indicates the changes of pH and Mn concentration during electrochemical coagulation as a function of the initial concentration. The results obtained from the experiments conducted with Mn exhibited that the type of anion influenced the Mn removal from liquid medium by electrochemical coagulation and the removal efficiency of Mn was lower than those in the other two metals. The Mn removal efficiency varied in the range of 40 and 43.5% in the presence of chloride as it was in the range of 55 and 65% in the presence of sulfate in bulk solution. The most fraction of the removed Mn occurred at first 5 min of electrocoagulation process in the experiments carried out with both anions. At all the experiments, the pH values increased during the EC process.

Consequently, these results showed that the priority order of the metals' removal by electrochemical coagulation was order of Cu > Zn > Mn. In addition, the results exhibited that the type of anion present in the solution rather than the initial concentration of metal ions further influenced the removal efficiency of metals. In contrast to our results, Merzouk et al. [10] reported that anions such as sul-

fates and acetates did not influenced the effectiveness of removal of different metal ions.

3.2. Effect of initial pH

The analysis of Cu indicated that all the initial pH conditions except of pH 7 resulted in similar behavior in pH variation. Huang et al. [12] reported that similar results for cadmium removal have been obtained. Additionally, it was observed that pH increased sharply to 8.66 and 8.86 within 5 min in the CC3 and CS3 at initial pH = 7, respectively. In the experiments conducted with Zn and Mn, pH variations exhibited similar trends in the existence of both sulfate and chloride anions. It was observed that pH decreased dramatically within 5 min particularly in MS3 and MC3 in the case of the initial pH > 6.0. Despite a decrease in pH, it increased again at progressive time intervals and reached about initial values at the end of the operation. This could be explained that electrocoagulation process exhibits buffering capacity because of the balance between the production and the consumption of OH^- which prevents high change in pH [14]. As a result, the presence of different anions did not generate an important distinction in the pH variations.

As illustrated in Fig. 4, the Cu^{2+} concentration in the bulk solution decreases dramatically with an increase in the initial pH. The removal efficiencies of Cu^{2+} remained very high when the initial pH was in the range of 5 and 9 in CS3. Overall removal reached about 100% within the first 5 min. The best removal results for copper were achieved with the chloride anion for pH values exceed 7. It was found that a retention time for 20 min was required to achieve an effective removal. Increasing the pH induced the high
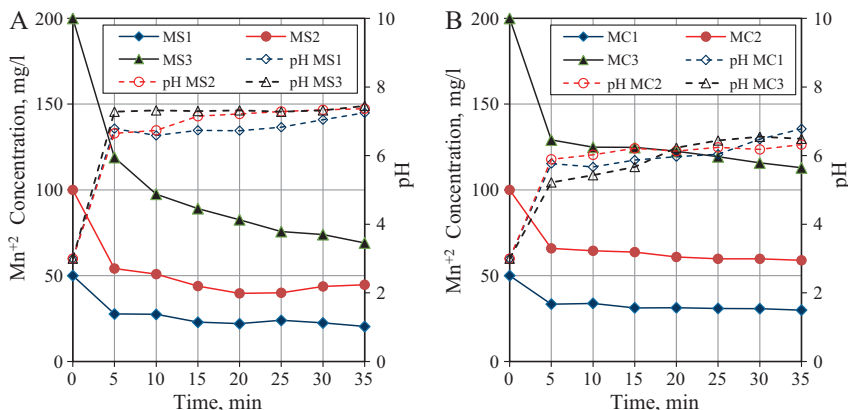

Fig. 3. Changes in manganese concentration and pH in the presence of (A) sulfate and (B) chloride as a function of initial concentration.
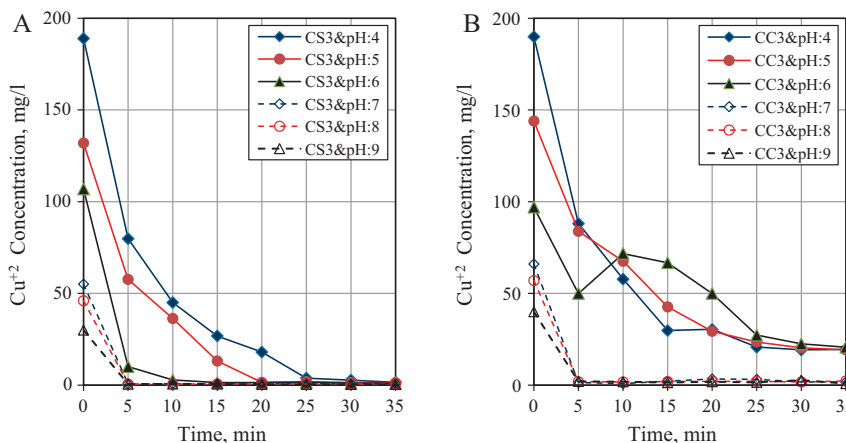
Fig. 4. Cu^{2+} profiles in the presence of (A) sulfate and (B) chloride as function of initial pH value and operating time.
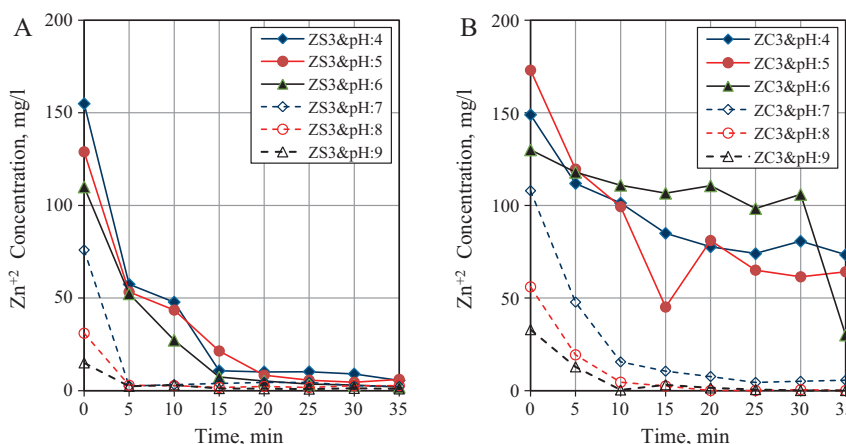

Fig. 5. Zn^{2+} profiles in the presence of (A) sulfate and (B) chloride as function of initial pH value and operating time.

removals of zinc in ZS3 and ZC3, as seen in Fig. 5. As observed by Adhoum et al. [5], the high removal efficiencies of Cu and Zn even at higher pHs might be ascribed to the precipitation of their hydroxides at the cathode, which start at pH 6–7 for copper and about 7–8 for zinc. On the other word, even at relatively low pH of the bulk electrolyte solution the removal rates of Zn and Cu high due to local high pH conditions that develop in the near cathode area. It is also important to explain that a certain amount of metals was precipitated by adjusting the initial pH before starting the

process, which causes the decreasing initial metal concentrations with increasing initial pH. We also considered this fact when the removal percentages of metals were calculated. Huang et al. [12] reported that all of aluminum species were converted to Al(OH)$_4^-$ being a water-soluble complex when pH values exceed 11. This soluble specie is useless for water treatment [18]. The pH values were always less than 11.0 in all the experiments. When chloride was the counter anion in solutions, the highest removal efficiencies for zinc were found to be 51, 63 and 77% at pH 4, 5 and 6, respectively.
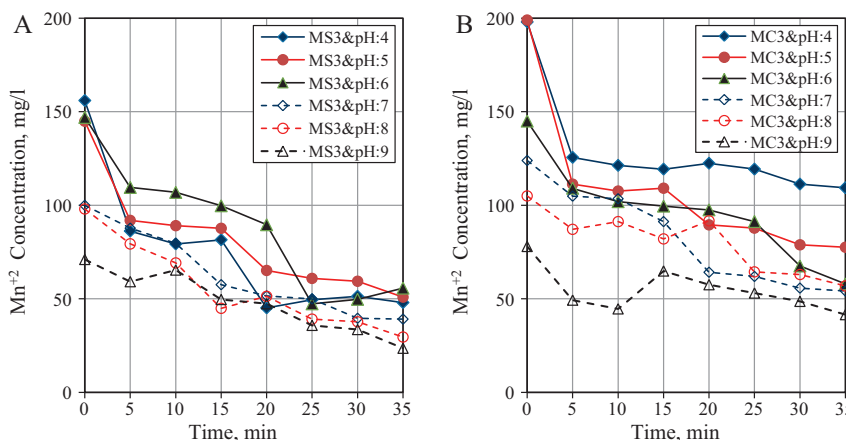

Fig. 6. Mn^{2+} profiles in the presence of (A) sulfate and (B) chloride as function of initial pH value and operating time.

This might be explained by the chemistry of the solution, because the mechanism of electrochemical coagulation is highly dependent on the chemistry of the aqueous solution. In previous studies, performance of electrochemical processes was found to be strongly affected by the presence of anions in the solution [19]. On the other hand, chemical dissolution of aluminum is affected by the pH, with much higher dissolution rates in basic solutions [9]. Considering these facts, it could be recognized that Cl^- could adversely influence the removals of zinc and copper at low pH values. As a result of many investigations on the subject [4,19], it has been argued that some characteristics have to be taken into account when aluminum electrodes are used. In contact with atmosphere, an insulating film alumina (Al_2O_3) develops on the electrode surface due to natural oxidation with oxygen gas. The surface oxide film, which is stable in the pH range 4–10 in aqueous media, has been reported to be constituted of an adherent compact layer covered with a more porous structure. The surface oxide layer complicates the formation of coagulating alumina cations. Additionally, in contrast to our results, several authors reported that the performance of the chloride solution was better when compared to sulfate solution in EC process [4,12,19].

As seen in Fig. 6, for both sulfate and chloride solutions higher initial pH resulted in higher removal efficiencies of Mn. The removal efficiencies of Mn increased by depending on the progressive time in the case of MS3, while they did not change very much in the case of MC3 over the time. It was observed that the lower removal efficiencies for Mn were determined with the solutions containing Cl^-. For instance, it was only 45 and 61% in the case of MC3 at pH 4 and 5, respectively. This can be explained by the pH variations observed in MS3 and MC3 that the lower pH values were measured when compared to those with the experiments of Cu and Zn.

4. Conclusions

It can be concluded from this study that the type of anion rather than the initial concentration of metal ions influenced significantly the removal efficiencies of metals. On the other hand, the presence of different anions did not generate an important difference between the pH variations during electrochemical coagulation. The best removals for three metals with different anions, sulfate and chloride, were received with increasing the pH. It was exhibited that the electrochemical coagulation was very effective especially for copper and zinc removal among the metals studied in this study. A treatment for 5 min accomplished more than 99.5% of copper and zinc when pH values exceed 7 in the existence of sulfate anion, while a treatment for 10 min was necessary to remove for zinc from the aqueous solution with chloride anion.

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