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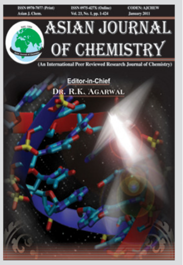

Removal of Zinc and Copper from Aqueous Solutions by Electrocoagulation Technology Using Iron Electrodes

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The aim of this study is to evaluate the batch electrocoagulation for the removal of zinc and copper from synthetic wastewater using iron electrodes with bipolar configuration. The effects of several working parameters, such as pollutant concentration (5, 50 and 500 mg L^{-1}), pH (3, 7 and 10), applied voltage (20, 30 and 40 V), reaction time (15, 30, 45 and 60 min), COD and turbidity were evaluated. The results indicated that the most effective removal capacities of studied metals (> 99.99 %) could be achieved when the applied voltage was kept equal 40 V. In addition, it is found that an increase in the applied voltage enhanced the speed of the treatment significantly. However, simultaneous increase of electrode and energy consumption was observed. Also consumed energy decreased with increase in zinc and copper concentration. Finally, the results demonstrated the technical feasibility of electrocoagulation as a reliable technique for removal of heavy metals from aqueous environments.

Key Words: Electrocoagulation, Zinc, Copper, Iron electrodes.

INTRODUCTION

Water quality and available quantity are being challenged by increased pollution from point and non-point sources such as industry and agriculture, respectively and the ever-increasing population[1]. Heavy metals, such as chromium, cadmium, copper, zinc and nickel, are contained in urban and industrial wastewater also landfill leachate, which pollutes the environment and strongly affects human health. In this regard, the prevention of environmental pollution has actively been studied[2-8]. Toxic heavy metals are released into the environment from a number of industries such as mining, plating, dyeing, automobile manufacturing and metal processing. The presence of heavy metals in the environment has led to a number of environmental problems[9-11]. In order to meet the water quality standards for most countries, the concentration of heavy metals in wastewater must be controlled[12,13]. Separation techniques of heavy metals, such as chromium, cadmium, copper, zinc and nickel, from industrial wastewater include precipitation, ion exchange, adsorption, electro-dialysis and filtration[14-16], but these techniques have limitations in selective separation and the problems of high investment cost and equipment operation[12]. During the past years, electrocoagulation method (EC) has been proposed as an effective method to treat various wastewaters such as landfill leachate, restaurant wastewater, saline wastewater, tar sand and oil shale wastewater, urban wastewater, laundry wastewater, nitrate and arsenic bearing wastewater and chemical mechanical polishing wastewater[15-20].

Electrocoagulation is a simple and efficient method to remove the flocculating agent generated by electro-oxidation of a sacrificial anode and generally made of iron or aluminum. This process 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 combines three main interdependent processes, operating synergistically to remove pollutants: electrochemistry, coagulation and hydrodynamics. In fact, in electrocoagulation process, the flocculating agent is generated by electro oxidation of a sacrificial anode, generally made of iron or aluminum. In this process, the treatment is done without adding any chemical coagulant or flocculants, thus reducing the amount of sludge which must be disposed[21]. An examination of the chemical reactions occurring in the electrocoagulation process shows that the main reactions occurring at the electrodes are:

$$Fe(s) \longleftrightarrow Fe^{3+}_{aq} + 3e^{-} \text{ (anode)} \tag{1}$$

$$3H_2O + 3e^{-} \longleftrightarrow 3/2H_{2\,g} + 3OH^{-}_{aq} \text{ (cathode)} \tag{2}$$

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

$$Fe^{3+}{}_{aq} + 3OH^{-}_{aq} \longleftrightarrow Fe(OH)_3 \tag{3}$$

The iron hydroxide flocs act as adsorbents and/or traps for pollutants and so eliminate them from the solution[22]. The main purpose of this research was to investigate of the electrocoagulation process efficiency for removal of zinc and copper from aqueous environments with iron electrodes and determination of the effects of voltage, pH, COD, turbidity, electrical conductivity and reaction time on the removal efficiency.

EXPERIMENTAL

At present study all chemicals including copper sulphate, zinc sulphate, sodium hydroxide pellets, concentrated sulfuric acid and potassium chloride were used as analytical grade. Desired concentrations of copper and zinc solutions (5, 50 and 500 mg L^{-1}) were prepared by mixing proper amount of copper sulphate and zinc sulphate with deionized water. In order to increase the conductivity of the solution to 1.6 mS cm^{-1}, potassium chloride (1 N) was added to the solution before injecting it into the apparatus. The chloro salt added to the solution can also prevent the formation of the oxide layer on the anode and therefore reduce the passivation problem of the electrodes. The pH of influent solution was adjusted to a desired value (3, 7 and 10) using H_2SO_4 and NaOH solutions (0.1 M).

Set-up and procedure: Experiments were performed in a bipolar batch reactor, with four iron electrode connected in parallel (bipolar mode). Only the outer electrodes were connected to the power source and anodic and cathodic reactions occurred on each surface of the inner electrode when the current passed through the electrodes. The internal size of the cell was 10 cm × 13 cm × 12 cm (width × length × depth) with an effective volume of 1000 cm^3. The volume (V) of the solution of each batch was 1 L. The active area of each electrode (plate) was 10 cm × 10 cm with a total area of 400 cm^2. The distance between electrodes was 1.5 cm. A power supply pack having an input of 220 V and variable output of 0-40 V (20, 30 and 40 V for this study) with maximum current of 5 ampere was used as direct current source. The temperature of each system was maintained at 25 ± 1 ºC. The pH values in influent and reactor unit were measured using a pH meter model E520 (Metrohm Herisau, Switzerland). A Jenway conductivity Meter (Model 4200) was employed to determine the conductivity of the solution. Different samples of 25 mL were taken at 15 min intervals for up to 1 h and filtered before being analyzed to determine the residual Zn^{2+} and Cu^{2+}. The residual Zn^{2+} and Cu^{2+} concentrations were determined using atomic absorption method according to the standard method[22]. During the runs, the reactor unit was stirred at 150 rpm by a magnetic stirrer to allow the chemical precipitate to grow large enough for removal. During electrocoagulation, an oxide film formed at the anode. In order to overcome electrode passivation at the anode, the electrodes were rinsed in diluted HCl solution (5 % v/v) after each experiment and rinsed again with tap water and finally weighted. All analyses were conducted in duplicate for reproducibility of data and all of the data in the figures and tables were the average ones.

RESULTS AND DISCUSSION

The electrocoagulation process is quite complex and may be affected by several operating parameters, such as pollutants concentrations, initial pH, applied voltage, COD and turbidity. In the present study, electrocoagulation process has been evaluated as a treatment technology for zinc and copper removal from synthetic solutions. Zinc and copper removal efficiency at different condition (pH, applied voltage and a variety of initial concentrations) in various times was evaluated.

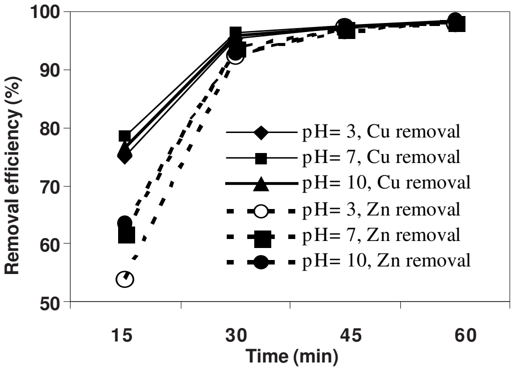
Effect of initial pH: It has been established in previous studies[23,24] that initial pH has a considerable effect on the efficiency of the electrocoagulation process. As observed by other investigators the pH of the medium changed during the process depending on the type of electrode material and initial pH. Meanwhile, EC process exhibits some buffering capacity, especially in alkaline medium, which prevents high changes in pH[25].

In this study, the pH was varied in the range 3-10 in an attempt to investigate the influence of this parameter on the removal of zinc and copper. Removal efficiencies of zinc and copper as a function of initial pH with iron electrodes are presented (Figs. 1-3). As observed by other investigators[26-28], a pH increase occurs when the initial pH is low (< 7). Vik *et al.*[26] ascribed this increase to hydrogen evolution at cathodes. Chen *et al.*[23] explained this increase by the release of CO_2 from wastewater owing to H_2 bubble disturbance.

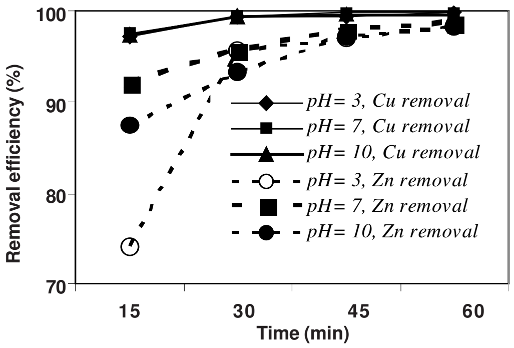
Indeed, at low pH, CO_2 is over saturated in wastewater and can release during H_2 evolution, causing a pH increase[29]. In addition, if the initial pH is acidic, reactions would shift towards a pH increase. In alkaline medium (pH > 8), the final pH does not vary very much and a slight drop was recorded. This result is in accord with previously published works[28,30-32] and suggests that the electrocoagulation can act as a pH regulator[31,33]. Hence, the final pH of treated wastewater was nearly neutral which allows it to be directly discharged in natural aquatic streams.

In this research, the influence of pH did not affect the removal efficiencies significantly over a wide range. Therefore, pH adjustment before treatment is not required in practical applications. The pH variation of solution after electrocoagulation process in various voltages showed that the final pH for pH 3, 7 and 10 of experiments is higher than initial pH, which is in agreement with previous results[34,35].

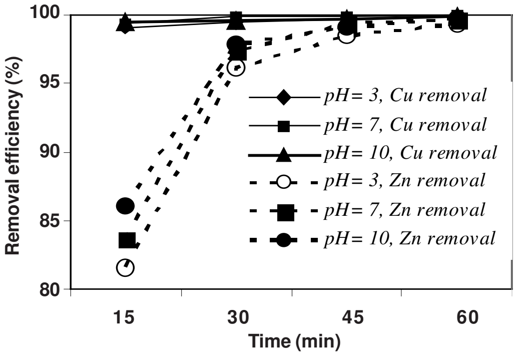
Effect of applied voltage: Preliminary laboratory testing of the electrolysis cell involved determining the effect of applied voltage on the efficiency of Zn^{2+} and Cu^{2+} removal. It is well-known that electrical current not only determines the coagulant dosage rate but also the bubble production rate and size and the flocs growth[36,37], which can influence the treatment efficiency of the electrocoagulation. Therefore, the effect of current density or applied voltage on the pollutants removal was investigated. The effect of the applied voltage on removal



(A) Voltage = 20 V

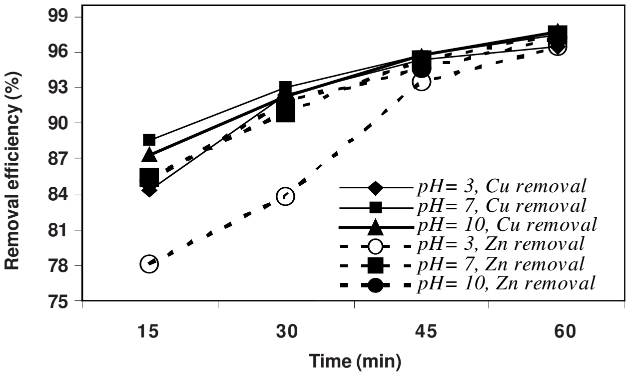


(B) Voltage = 30 V

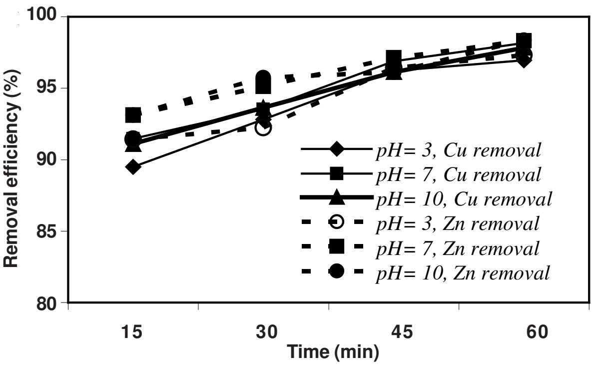


(C) Voltage = 40 V

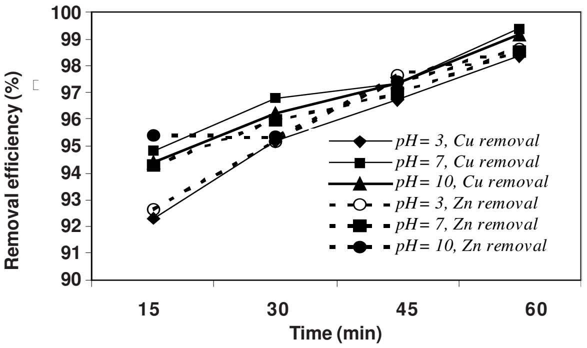
Fig. 1. Effect of pH and retention time on Zn and Cu removal by electrocoagulation using iron electrodes (Zn and Cu concentration = 5 mg/L)



(A) Voltage = 20 V

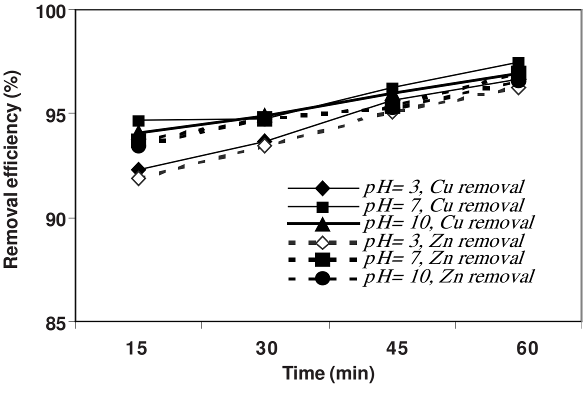


(B) Voltage = 30 V

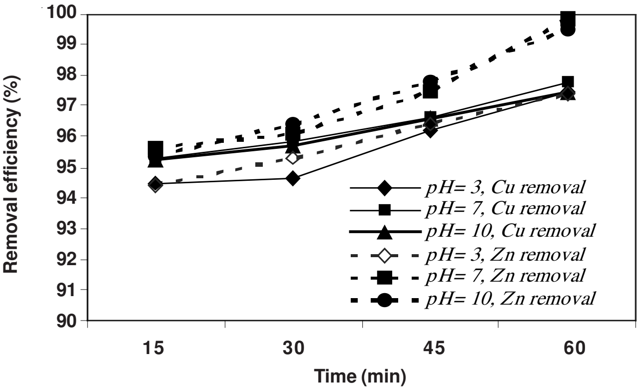


(C) Voltage = 40 V

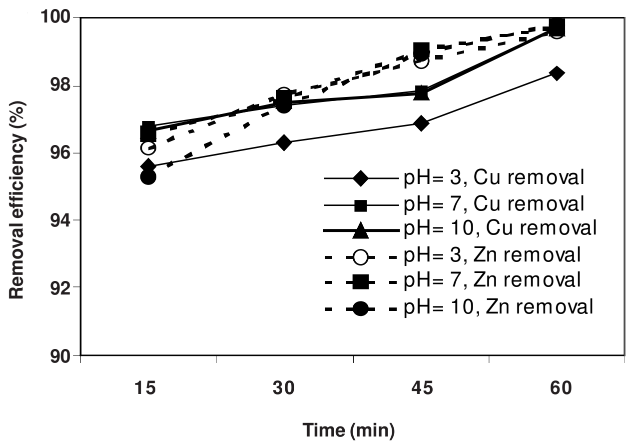
Fig. 2. Effect of pH and retention time on Zn and Cu removal by electrocoagulation using iron electrodes (Zn and Cu concentration = 50 mg/L)



(A) Voltage = 20 V



(B) Voltage = 30 V



(C) Voltage = 40 V

Fig. 3. Effect of pH and retention time on Zn and Cu removal by electrocoagulation using iron electrodes (Zn and Cu concentration = 500 mg/L)

efficiency is shown in Figs. 1-3. It can be seen that an increase in the applied voltage from 20-40 V led to an increase in the Zn^{2+} and Cu^{2+} removal efficiency.

The highest applied voltage (40V) produced the quick treatment with > 90 % reduction only after 15 min (for all concentrations) and the lowest Zn^{2+} and Cu^{2+} removal efficiency occurred in the lowest applied voltage (20 V) and initial concentrations of 5 mg L^{-1}. This is ascribed to the fact that for higher voltage, the amount of iron oxidized increased, resulting in a greater amount of precipitate for removal of pollutants. In addition, it was demonstrated that bubbles density increases and their size decreases with increasing current density[38,39], resulting in a greater upwards flux and a faster removal of pollutants and sludge flotation. As the current decreased, the time needed to achieve similar efficiencies increased and the results of this research confirm this fact. This expected behaviour is explained by the fact that the treatment efficiency was mainly affected by charge loading (Q = It), as reported by Chen[24]. However, the cost of the process is determined by the consumption of the sacrificial electrode and the electrical energy which economically are the advantages of this method. These results suggest 40 V as an optimal applied voltage for the treatment of effluents containing zinc and copper, since it ensures the quick removal rate with the lowest cost.

Effect of initial concentration: A set of experiments were performed with different initial concentrations of zinc and copper to determine the time required for removal under various conditions of electrocoagulation process. The results obtained at different applied voltage showed that initial concentration of Zn^{2+} and Cu^{2+} can not effect significantly on efficiency removal and for higher concentration of Zn^{2+} and Cu^{2+}, lower applied voltage is needed. On the other hand, there is not a direct correlation between pollutant concentration and removal efficiency. It is clear from Figs. 1-3 that in the higher concentrations, longer time is needed for removal of zinc and copper, but higher initial concentrations of zinc and copper were reduced significantly in relatively less time than lower concentrations. The time taken for reduction thus increases with the increase in concentration. This can be explained by the theory of dilute solution. In dilute solution, formation of the diffusion layer at the vicinity of the electrode causes a slower reaction rate, but in concentrated solution the diffusion layer has no effect on the rate of diffusion or migration of metal ions to the electrode surface[39,40].

Effect of electrocoagulation time: The time dependence of zinc and copper removal by electrocoagulation process at different pH is shown in Figs. 1-3. It can be seen from the figures that up to 53-99 % of the initial concentration of zinc and copper decreased within 15-30 min of processing for all concentrations. These results are according to colour removal efficiency in 20 min (at least 80 %) reported by Chou *et al.*[42]. Also, the residual Zn^{2+} and Cu^{2+} concentrations in effluent at the end of reaction time (1 h) reached to standard range so we can discharge treated effluents to the environment in safety. Comparison of Zn^{2+} and Cu^{2+} removal efficiency (Figs. 1-3) showed that removal efficiency is similar.

Effect of COD and turbidity: A set of experiments were performed with different initial concentrations of Zn^{2+} and Cu^{2+} (5, 50 and 500 mg L^{-1}) to evaluate the effect of COD (with initial concentration 100, 500 and 1000 mg L^{-1}) and turbidity (10, 50 and 200 NTU) in wastewater on the removal efficiency of Zn^{2+} and Cu^{2+}. The results obtained at selected condition (pH = 7, reaction time = 1 h and voltage = 40 V) showed that removal efficiency for various concentrations of zinc and copper was unchanged and hence electrocoagulation process can be apply efficiently for Zn^{2+} and Cu^{2+} removal in presence of COD and turbidity.

Electrode consumption: With regard to a series of tests conducted with different concentration of zinc and copper in the solution, the weight of the consumed electrode with respect to different applied voltages is given in Table-1. As it is presented in the table, the iron electrode consumption varied between 1.2 and 6.6 g L^{-1} for Zn^{2+} removal and 1.5 and 12.8 g L^{-1} for Cu^{2+} removal. When the applied voltages of the system were increased from 20-40 V, the consumed iron electrode increased from 2.1-6.3 and 4.2-10.6 g L^{-1} for Zn^{2+} and Cu^{2+} removal, respectively (with initial concentration = 5 mg L^{-1}). It can be concluded that the higher voltage of the system applied, the weight of the electrode consumed in the process has been increased and also the higher the concentrations of the Zn^{2+} and Cu^{2+} in the solution, the higher consumption of the electrode is would be. As the tables represents consumed electrode with 40 V in the process is much more than the process conducted with 20 V. As, zinc and copper concentrations in the solution increased to 500 mg L^{-1}, the consumption of electrode did not increase as much, but the zinc and copper removal efficiency has taken place, because much flocs formation helped to sweep away zinc and copper and there was no need for as much electrode consumption as before. For example, iron electrode consumption for initial concentration of zinc and for 5 mg L^{-1} and voltage 40 V was 6.3 g while for initial concentration of 500 mg L^{-1} it was 2.9 g.

Electrical energy consumption: In addition to removal efficiency, energy consumption was also taken into consideration. The relationship between energy consumption and pollutant concentration at various pH is presented in Table-2. The energy consumption with iron electrodes varied between

TABLE-1
IRON ELECTRODE CONSUMPTION DURING ELECTROCOAGULATION PROCESS (g/L)

Voltage (V)	Zinc conc. (mg/L)			Copper conc. (mg/L)		
	5	50	500	5	50	500
20	2.1	1.9	1.2	4.2	1.9	1.5
30	3.6	3.8	2.3	8.1	5.6	1.6
40	6.3	6.6	2.9	10.6	7.8	12.8

TABLE-2
ELECTRICAL ENERGY CONSUMPTION DURING ELECTROCOAGULATION PROCESS (kWh/g), AT VOLTAGE = 40 V

pH	Zinc conc. (mg/L)			Copper conc. (mg/L)		
	5	50	500	5	50	500
3	19.42	2.11	0.12	32.74	2.58	0.16
7	18.17	2.57	0.08	34.12	2.43	0.48
10	22.31	1.73	0.17	35.63	2.19	0.71

0.08 and 22.31 kWh g^{-1} for Zn^{2+} removal and 0.16 and 35.63 KWh g^{-1} for Cu^{2+} removal. It can be concluded that consumed energy decrease with increase in Zn^{2+} and Cu^{2+} concentration, because the enhanced floc formation help sweep pollutant away from the solution. Also at present study more energy consumed for Cu^{2+} removal. These results are according to Zn^{2+} and Cu^{2+} removal efficiency by aluminum electrodes that reported by Nouri *et al.*[41].

Conclusion

In this work it was shown that electrocoagulation process achieves a fast and effective reduction of pollutants (Zn^{2+} and Cu^{2+}) present in industrial wastewaters. The results obtained with synthetic wastewater revealed that the most effective removal capacities of proposed metals (> 99.99 %) achieved at 40 V applied voltage. In addition, the increase of applied voltage, in the range of 20-40 V, enhanced the treatment rate without affecting the charge loading required to reduce metal ion concentrations under the admissible legal levels. In this process, the pH neutralization effect made its effective in a much wider pH range, which made it superior to traditional chemical coagulation. On the other hand, the final pH of treated wastewater was nearly neutral which allows it to be directly discharged in natural aquatic streams. The process was successfully applied to the treatment of a tannery wastewater where an effective reduction of zinc and copper concentration under legal limits was obtained. Finally, the results demonstrated the technical feasibility of electrocoagulation as a reliable technique for removal of heavy metals from aqueous environments.

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