Removal of Heavy Metals (Cd, Cu, Ni) by Electrocoagulation

Umran Tezcan Un and Sadettin Eren Ocal

***Abstract*—In this study, removal of cadmium (Cd), copper (Cu) and nickel (Ni) from a simulated wastewater by electrocoagulation (EC) method using batch cylindrical iron reactor was investigated. The influences of various operational parameters such as initial pH (3, 5, 7), current density (30, 40, 50 mA/cm^2) and initial heavy metal concentration (10, 20, 30 ppm) on removal efficiency were investigated. It was seen from the results that removal efficiencies were significantly affected by the applied current density and pH. The experimental results indicated that after90 minutes electrocoagulation the highest Cd, Ni, Cu removal of 99.78%, 99.98%, 98.90% were achieved at the current density of 30 mA/cm^2 and pH of 7 using supporting electrolyte (0,05 M Na_2SO_4) respectively. The experimental results revealed that the removal of heavy metal ions by our design electrochemical cell can be successfully achieved.**

***Index Terms*—Heavy metal removal, electrocoagulation, treatment.**

I. Introduction

The presence of heavy metals in water and wastewater causes serious environmental and health problems because of their solubility in water. Although organic contaminants can be biodegradable, inorganic pollutants cannot be biodegradable and they can enter to the food chain and accumulate in living organisms.

Heavy metals like copper, nickel, lead and zinc are resulted from several sources such as metal and processing industries, batteries, fertilizer and pesticides.

Pure nickel shows a significant chemical activity. More than adequate nickel accumulation may be resulted with serious lung, kidney and skin problems [1]. Although copper does not affect body in small concentration, high amount copper accumulationmay be resulted with toxic reactions like puking, cramps and spasms which may lead to death [2]. Cadmium has been classified by U.S. Environmental Protection Agency as a probable human carcinogen. The drinking water guideline value recommended by World Health Organization (WHO) is 0.005 mg/L Cd [3]. Due to the adverse effects on the environment and human health, usage of cadmium is restricted in Europe.

In spite of the fact that electrocoagulation is not a new technology which has been known from 19th centuries, electrocoagulation hasn't been widely applied because of relatively large capital investment, expensive electricity requirement. However, electrochemical technologies have turned back since it is eco-friendly technology [4], [5].

In this study, the removal of nickel, cadmium and copper from the simulated solution was investigated using iron electrodes by electrocoagulation(EC). Experiments were performed to determine the effects of varying operational parameters such as; initial pH, current density and initial concentration on metal removal efficiency. Also, electrical energy consumption (EEC) was calculated to give an opinion about estimated cost of EC process.

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II. Electrocoagulation (EC) Process

EC is an electrochemical process with reactive anode and cathode (iron or aluminum electrode). When current is applied to the systemby a power supply, metallic ions are dissolved from anode and transferred to the bulk. Afterwards metallic ions combine into larger flocs and can be removed easily[6].Water molecules are hydrolyzed at the cathode, simultaneously. Two different mechanism proposed for iron electrodes can be seen in the reactions (1)-(6).

Mechanism I
In the anode:

$$4\ Fe_{(s)} \rightarrow 4\ Fe^{2+}_{(aq)} + 8e^- \quad (1)$$

In the cathode:

$$8\ H^+_{(aq)} + 8\ e^- \rightarrow 4\ H_{2(g)} \quad (2)$$

In the solution:

$$4\ Fe^{2+}_{(aq)} + 10\ H_2O_{(l)} + O_{2(g)} \rightarrow 4\ Fe(OH)_{3(s)} + 8\ H^+_{(aq)} \quad (3)$$

Mechanism II
In the anode :

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \quad (4)$$

In cathode:

$$2\ H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2\ OH^-_{(aq)} \quad (5)$$

In solution:

$$Fe^{2+}_{(aq)} + 2\ OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)} \quad (6)$$

Metal ions produced at the anode and hydroxide ions produced at the cathode react in the aqueous media to produce various hydroxides species depending on the pH such as $Fe(OH)_2$, $Fe(OH)_3$, $Fe(OH)^{2+}$, $Fe(OH)^{2+}$ and $Fe(OH)_4^-$. The iron-hydroxides coagulate and precipitate to the bottom of system [7].

To determine theoretical dissolved mass of iron from anode, Faraday's law shown in equation (7) can be used.

$$m = \frac{I \times t \times M}{z \times F} \quad (7)$$

where *m* is the amount of anode material dissolved (g), *I* is

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the current (A), t is the electrolysis time (sec), M is the molecular weight (g/mol), z is the number of electrons involved in the reaction, and F is the Faraday's constant.

The electrocoagulation of cadmium ion was studiedusing four plate aluminum electrode by the Mahvi and Bazzrafshan [8], using five pair of aluminum electrodesby Bayar *et al*. [9], using aluminum anode and cathode by Vasudevan *et al*. [6], and by Mansour *et al*. [10]. Removal of Ni and Cr from tap water was studied with aluminum electrodes by Hernández, *et al*. [11]. The removal of nickel and cobalt was also studied using two aluminum plates by Mansour and Hasieb [12]. The removal of Ni (II), Pb (II), Cd (II) ions was studied using an assorted electrode sets of aluminum and ironby Khosa *et al.* [13]. Rajemahadik, *et al.* [14] were also studied the removal of heavy metals from water including Ni, Cr, Zn using Fe and Al electrodes.

III. Materials and Methods

A. Reagents and Solutions

A stock solution of metal ions with the concentration of 1000 mg/L was prepared from $Cd(NO_3)_2\,4H_2O$, $Cu(NO_3)_2\,3H_2O$, $Ni(NO_3)_2\,6H_2O$. Required initial concentrations were preparedby diluting the stock solution. To increase the conductivity of the solution, 0.05M Na_2SO_4 (Merck) was added before the experiments. The pH of the solution was arranged using 1N H_2SO_4 (Merck)

B. Procedure in Batch Operation

In the experimental study the uniquely designed batch EC reactor shown in the Fig. 1 was used. The iron cylindrical reactor operated as a cathode has height of 10cm and an internal diameter of 10.3 cm. The stirrer has three iron blades with width of 0.9cm and length of 7cm, and operated as an anode. Anode was stirred the solution to maintain uniform composition at 100 rpm with a mechanical stirrer (Jeo Tech). In each experiment, 0.5 L of solution was poured into the cylindrical cathode and operation was started with by switching the DC power supply (Statron 2257) on.

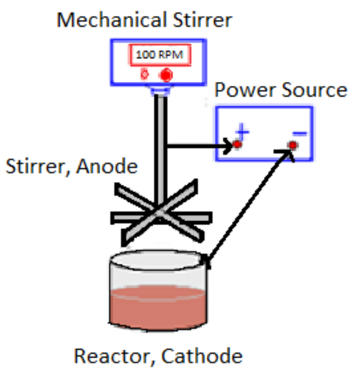

Fig. 1. Experimental set-up.

C. Analyses

In the experiments, 5 ml of sample were taken from the reactor at the 15 min intervals and filtered. The concentrations of metal ions were determined using atomic adsorption (Varian Spectra A 250 Plus). All samples were analyzed in duplicate to ensure data reproducibility, and an additional measurement was carried out, if necessary.

The removal efficiency (RE %) after EC was calculated using the following equation;

$$\mathrm{RE}\% = \frac{(C_O - C)}{C_O} \times 100 \tag{8}$$

where C_o and C are the concentrations of metal ions before and after EC, respectively, in ppm.

Electrical energy consumption (E_c; kWh/m^3) was also calculated using Eq. 9.

$$E_C = \frac{V \times I \times t}{v_W} \tag{9}$$

where V is Voltage (V), I is Current (A), t is operation time(h), and v_w is the volume of the wastewater (m^3).

IV. Results and Discussion

A. Effect of Initial pH

pH is one of the effective operational parameters in the electrocoagulation process.Effect of initial pH was investigated using the initial pH values of 3, 5, 7atthe current density of 40mA/cm^2 and initial ion concentration of 20 ppm. As can be seen from Fig. 2 the highest removal of Cd was obtained at pH 7. The initial Cd concentration of 20 ppm was reduced to the 0.16 ppm with the removal efficiency of 99.2 %after 90 minutes EC. As seen from the Fig. 3 and Fig. 4, pH has no significant effect on the removal efficiencies for the electrocoagulation of Cu and Ni. The removal efficiencies at pH 7 for the Cu and Ni were 98.3% and 99.8%, respectively. The removal of Ni and Cu were increased with the time within the first 15 minutes. After that time, removal efficiencies scarcely increased as seen from Fig. 3 and Fig. 4.

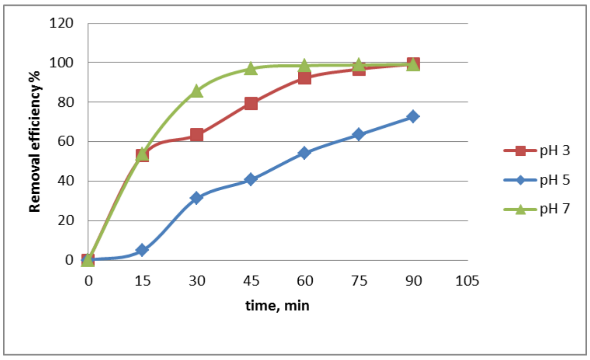

Fig. 2. Effect of pH on Cd removal efficiency (current density: 40mA/cm^2, initial concentration: 20 ppm).

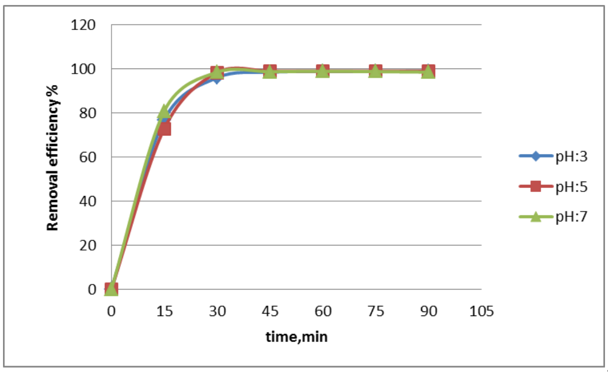

Fig. 3. Effect of pH on Cu removal efficiency (current density: 40mA/cm^2, initial concentration: 20 ppm).

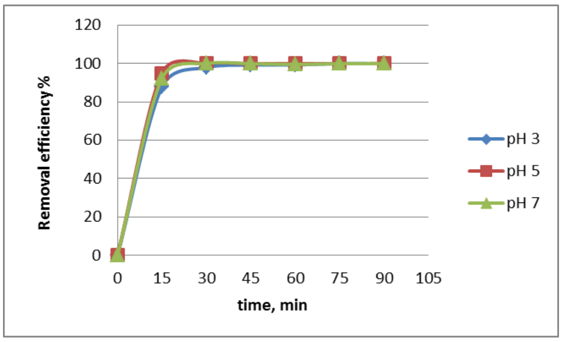

Fig. 4. Effect of pH on Ni removal efficiency (current density: 40mA/cm^2, initial concentration: 20 ppm).

Similarly the best results was obtained at pH 7 by Khosa *et al.* [13], Vasudevan *et al.* [6], Kumarasinghe *et al.* [15]and Kamaraj *et al.* [16] for the removal of heavy metal.

B. Effect of Current Density

The current density is an effective parameter that controls the reaction rate in the electrochemical systems, and it determines the amount of Fe^{2+} ions released by the anode.

To determine the effect of current density, experiments were performed at initial pH of 7 and initial metal concentrations of 20 ppm. After 90 min EC the initial Cd concentration of 20 ppm was reduced to 0.04, 0.16 and 0.28ppm with the removal efficiencies of 99.8%, 99.2% and 98.6% at the current densities of 30, 40 and 50 mA/cm^2, respectively as seen from Fig. 5. After 60 min EC, the removal efficiencies are almost constant. Therefore, the electrocoagulation process should be ended to reduce energy consumption.

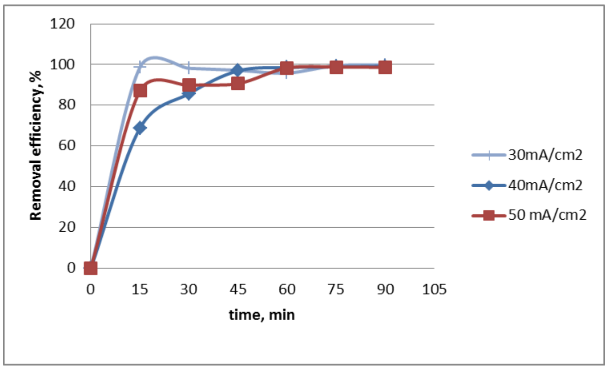

Fig. 5. Effect of current density on Cd removal efficiency (pH: 7, initial concentration: 20 ppm).

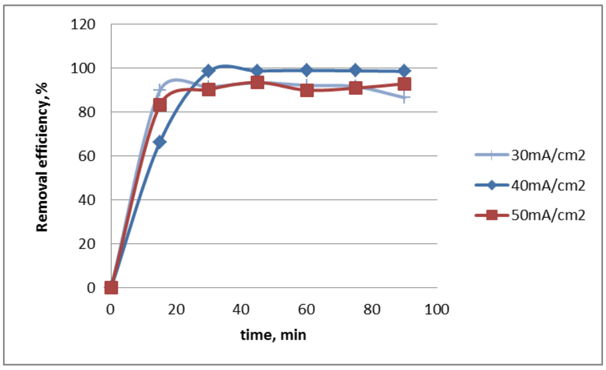

Fig. 6. Effect of current density on Cu removal efficiency (pH: 7, initial concentration: 20 ppm).

Similarly, the removal of copper ion increase with the increasing of current density as seen from the Fig. 6. Kamaraj *et al.* [16] also obtained similar results. They obtainedthe removal efficiency of 97% forthe initial copper concentration of 10 mg/L and 96% forthe initial copper concentration of 50 mg/L at current density of 30 mA/cm^2. The same magnitude of removal efficiencies were obtained for the removal of copper, lead, and cadmium by Kumarasinghe *et al.* [15].

As seen from Fig. 7, 30 min electrocoagulation was satisfied for the removal of Ni with the removal efficiency of 99% at 30 mA/cm^2. After this time, removal efficiency was not changed significantly. Mansour and Hasieb [12], obtained 93% efficiency at 30 mA/cm^2 after 35 min EC while removal efficiency of 99% obtained at 40 mA/cm^2.

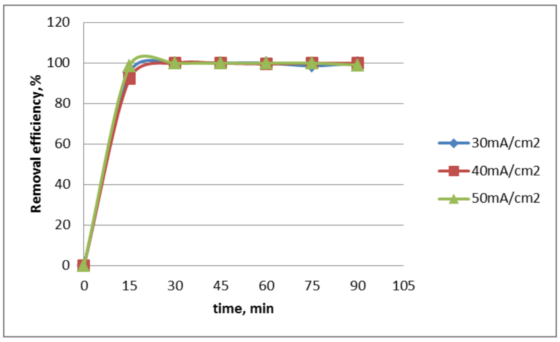

Fig. 7. Effect of current density on Ni removal efficiency (pH: 7, initial concentration: 20 ppm).

The variation of electrical energy consumption with current density can be seen from Fig. 8 for Cd. As seen from Fig. 8, the electrical energy consumption was increased with the increasing current density because of the increase in applied voltage. Similar behaviors were also observed for the removal of Cu and Ni (data not shown).

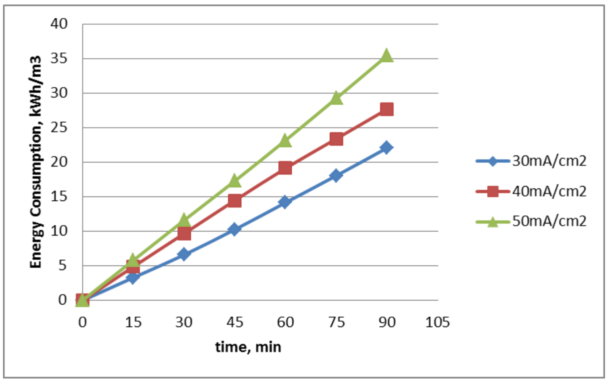

Fig. 8. Effect of current density on energy consumption (pH: 7, initial concentration: 20 ppm).

C. Effect of Initial Concentration

The effect of initial concentration was investigated using metal ion concentrations of 10 to 50 mg/L at the current density of 30mA/cm^2 and pH of 7.

Fig. 9 shows the variation of Cd concentration with the various initial concentrations as a function of time. The removal efficiencies were 99%, 99% and 97% at the initial concentrations of 10, 20 and 50 ppm Cd, respectively after 75 min EC. Khosa *et al.* [13] studied removal of heavy metal from water using electrocoagulation at pH 7 using aluminum and iron electrodes. They got better results using iron electrode with the removal efficiency of 80% in 10 minutes EC while removal efficiency of 87% was obtained in 15 min in our system.

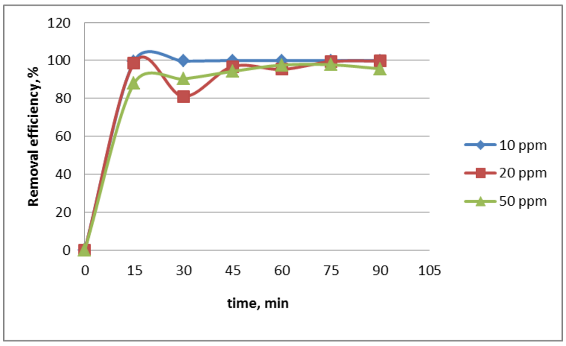

Fig. 9. Effect of initial concentration on Cd removal efficiency (pH: 7, current density: 30mA/cm^2).

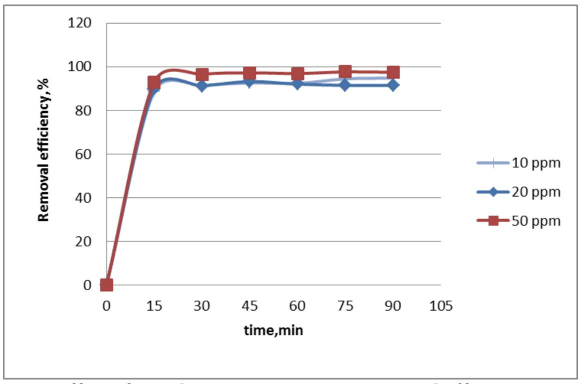

Fig. 10. Effect of initial concentration on Cu removal efficiency (pH: 7, current density: 30mA/cm^2).

The effect of initial concentration of Cu and Ni can be seen from Fig. 10 and Fig. 11 at 30mA/cm^2 and pH 7. As can be seen from the Fig. 10 and Fig. 11, higher initial concentrations caused higher removal rates of metal ions. The removal efficiencies were 92, 92 and 96% for the initial concentrations of 10, 20 and 50 ppm Cu, respectively at the end of 60 min EC operation. The removal efficiencies higher than 99.97% were obtained for the removal of Ni at all initial concentrations.

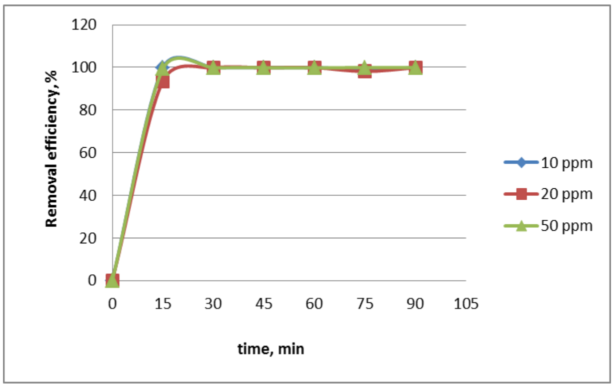

Fig. 11. Effect of initial Concentration on Ni Removal Efficiency (pH: 7, current density: 30mA/cm^2).

V. Conclusion

In this study, the removal of Cd, Cu, Ni from simulated wastewater by electrocoagulation using iron sacrificial electrodes was investigated. The effects of current density, initial pH, and initial metal concentrationon the removal efficiency were examined in cylindrical electrochemical reactor.

The following conclusions could be drawn from the present study:

1) The experimental results revealed that the removal of heavy metal ions by our design electrochemical cell can be successfully achieved.
2) The results obtained at varying operation conditions in order to elucidate their effects on process performance implied that removal efficiencies were significantly affected by the applied current density and pH.
3) The experimental results indicated that the highest Cd, Ni, Cu removal of 99.78%, 99.98%, 98.90% were achieved with a current density of 30 mA/cm^2 at the 0,05 M Na_2SO_4 electrolyte concentration and pH of 7 end of 90 minutes electrocoagulation operation.

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