REMOVAL OF CADMIUM FROM INDUSTRIAL EFFLUENTS BY ELECTROCOAGULATION PROCESS USING IRON ELECTRODES

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ABSTRACT

The object of this study is the evaluation of cadmium removal from industrial wastewater by electrocoagulation process. For this study a glass tank in 1.56 L volume with four plate electrode was used to do experiments. The electrodes made of iron and connect to the positive and negative pole of DC power supply (bipolar mode). The tank was filled with synthetic wastewater that was containing cadmium ion in concentration 5, 50 and 500 mg/L and then it was started up. The percent of cadmium ion removal was measured at pH 3, 7 and 10 and in electric potential range of 20, 30 and 40 volts. At the end of each stage of experiment, volume of produced sludge was measured. The results obtained at different electrical potential showed that initial concentration of cadmium can effect on efficiency removal and for higher concentration of cadmium, higher electrical potential or more reaction time is needed. On the other hand, if the initial concentration increases, the time required of process should increase too. The final pH for iron electrodes was always higher than initial pH. As expected, the results showed that for a given time, the removal efficiency increased significantly with increase of current density. The highest electrical potential (40V) produced the quickest treatment with >99% cadmium reduction occurring after only 20 min. The result showed that, in this process, the use of different electrical potentials can provide a wide range of pH for doing this process and electrocoagulation process (using iron electrodes) is a reliable, safety, efficient and cost-effective method for removal of cadmium from industrial effluents, especially designed for pH =10 and voltage = 40V.

Key words : Electrocoagulation process, cadmium removal, Iron electrodes, industrial effluents

INTRODUCTION

Heavy metal species are some of the most common pollutants that are found in industrial wastewaters. Because of their toxicity, these species can have a serious impact if released into the environment as a result of bioaccumulation, and they may be extremely toxic even in trace quantities. One such a heavy metal, cadmium, along with its compounds, is widely used in pigments, as heat stabilizers for plastics, for corrosion resistance of steel and cast iron, metal plating, phosphate fertilizer, mining, pigments, alloy industries, in soldering and brazing, and in the battery industry (Ni-Cd batteries). Cadmium is highly toxic and there is some evidence that it is carcinogenic (Hiatt and Huff, 1975). The harmful effects of Cadmium include a number of acute and chronic disorders, such as "itai-itai" disease, renal damage, emphysema, hypertension, and testicular atrophy (WHO, 1984; Leyva-Ramos, 1997).

When ingested by human beings, cadmium that is not excreted immediately has a long half-life of several hundred days, so that a low dose exposure over a long period of time can lead to a high body burden. In view of its persistence as a cumulative poison and the low tolerance of the human body towards cadmium, it is of interest to develop schemes for the removal of heavy metals from wastewaters prior to their disposal. Such disposal is, of course, subject to strict environmental regulation. In the case of cadmium, for example, the immobilization and remobilization of Cd(II) by ferrihydrite, and the effect of Cd(II) on the

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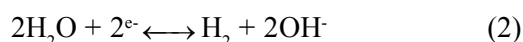Tel: +98 21 8895 4914, Fax: +98 21 8895 0188

conversion of ferrihydrite to goethite and hematite has been reported previously (Sun *et al.*,1996 ; Lin *et al.*, 2000) . The drinking water guideline value recommended by World Health Organization (WHO) is 0.003 mg Cd/L (WHO, 2003).

A variety of specialized treatment processes for the removal of heavy metals prior to their discharge into the environment have been developed (Clifford *et al.*, 1986). Among them, the simple process of metals as insoluble hydroxides, carbonates, or sulfides is used in about 75% of electroplating facilities to treat wastewater (Karthikeyan *et al.*, 1996). Of all the treatment techniques, heavy metal hydroxide process is the most commonly employed because of its low cost and simplicity. This process is as simple as increasing the pH of the effluent using lime (CaO) or caustic soda (NaOH) to precipitate and hence immobilize the heavy metals as their respective hydroxides. However, there are some problems and difficulties with this method including producing much sludge and also disposal of this sludge and the owners of industry have some difficulties with these two problems (Patterson, 1985; Karthikeyan *et al.*, 1996). Another way for cadmium removal from industrial wastewater is electrocoagulation process which is without any chemical material using and only uses transferring iron ion's electron to cadmium in the form of metal. In this method, cadmium precipitates and remove and finally we can recycle it and use it in the production cycle again. In the electrocoagulation (EC) cell, iron anodes dissolve and produce Fe^{2+}. The following shows the major reactions taking place in the EC cell (Kongsricharoern and Polprasert, 1995):
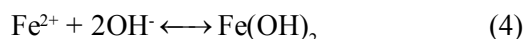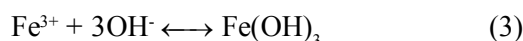
Anode (oxidation):

$$Fe \longleftrightarrow Fe^{2+} + 2e^- \qquad (1)$$

Cathode (reduction):

$$2H_2O + 2e^- \longleftrightarrow H_2 + 2OH^- \qquad (2)$$

Co-precipitation:

$$Fe^{3+} + 3OH^- \longleftrightarrow Fe(OH)_3 \qquad (3)$$
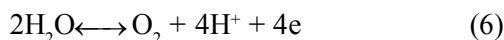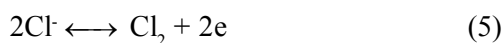
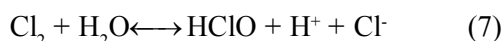$$Fe^{2+} + 2OH^- \longleftrightarrow Fe(OH)_2 \qquad (4)$$

If the anode potential is sufficiently high, secondary reactions may occur at the anode, such as direct oxidation of organic compounds and of H_2O or Cl^- present in wastewater:

$$2Cl^- \longleftrightarrow Cl_2 + 2e \qquad (5)$$

$$2H_2O \longleftrightarrow O_2 + 4H^+ + 4e \qquad (6)$$

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

$$Cl_2 + H_2O \longleftrightarrow HClO + H^+ + Cl^- \qquad (7)$$

$$HClO \longleftrightarrow ClO^- + H^+ \qquad (8)$$

The goal of this research was to study the efficiency of electrocoagulation process to removal of cadmium from industrial effluents (such as plating bath wastewater) with iron electrodes and determination of the effects of voltage, pH and reaction time on the removal efficiency of cadmium.

MATERIALS AND METHODS

This study has been conducted in the environmental chemistry laboratory of School Health of Tehran University of Medical Sciences in late 2006. All chemicals including cadmium nitrate, sodium hydroxide pellets, concentrated sulfuric acid and potassium chloride were used as received from Merck Company. Desired concentrations of cadmium solution were prepared by mixing proper amount of cadmium nitrate with deionized water. In order to increase the conductivity of the solution to 1.6 mS/cm, potassium chloride (1 N) was added to the solution before injecting it into the apparatus. The chloride 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 by using sulfuric acid solution and sodium hydroxide (0.1 M). Experiments were performed in a bipolar batch reactor (Fig. 1), with four iron electrodes 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 × 13cm × 12 cm (width × length × depth) with an effective volume of 1000 cm³. The volume (V) of the
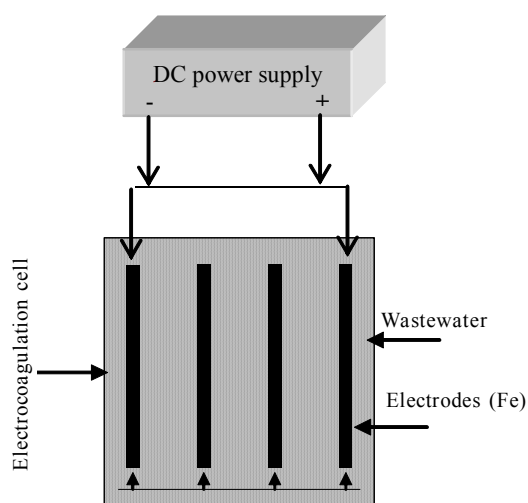
Fig. 1: A schematic diagram of the experimental set up

solution of each batch was 1 l. The active area of each electrode was 10×10 cm. The distance between of electrodes was 1.5 cm. respectively. A power supply pack having an input of 220V and variable output of 0–40V with maximum current of 5 ampere was used as a direct current source. 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. Samples were extracted every 20 minute and then immediately filtered through a 0.45-µm mixed cellulose acetate membrane. The residual cadmium concentration was determined using Atomic Absorption method according to the standard method (APHA, 1992). The percent of cadmium ion removal was measured at pH 3, 7 and 10 and in electrical potential of 20, 30 and 40 volts. Also at the end of each stage of experiment, volume of produced sludge was measured. In order to study the effect of turbidity on chromium removal by electrocoagulation process, a set of experiments with different initial concentration of turbidity (10, 50 and 200 NTU) were performed under optimum conditions (pH=3, Time=60 min, Voltage= 40 V). Standard solution of turbidity was prepared by dissolving 5.00 g of hydrazine sulfate and 50.0 g of hexamethylenetetramine in one liter of distilled water. This solution is equal to 4000 NTU. Then this stock turbidity solution was added to increase

chromium solution turbidity until 10, 50 and 200 NTU values are attained. In order to study the effect of organic matter presence (such as COD) on chromium removal by electrocoagulation process, a set of experiments with different initial concentrations of COD (100, 500 and 1000 mg/L O_2) were performed under optimum conditions (pH=3, Time=60 min, Voltage= 40 V). Standard solution of COD was prepared by dissolving 8.502 g of Potassium hydrogen phthalate ($KC_8H_5O_4$) in distilled water and diluted to 1000 mL. The prepared solution has a theoretical COD value of 10000 mg/L.

RESULTS

The results of cadmium removal for various initial concentrations 5, 50 and 500 mg/L, by electrocoagulation process using iron electrodes are shown in Tables 1-3. The results of these Tables illustrate that cadmium removal efficiency for different conditions such as initial pH and electrical potential is significant (>90%). Table 4 illustrates the results of consumed iron electrode during electrocoagulation process for various pH and cadmium initial concentrations. With increase in electrical potential (voltage), the amount of electrode consumption increased, too. So, the highest electrode consumption observed at electrical potential 40V. Table 5 shows amount of consumed energy during electrocoagulation process at voltage 40V and for different initial concentrations of cadmium. These results illustrated that consumed energy decreased with increase in cadmium initial concentration.

Table 1: Percent of cadmium removal during electrocoagulation process using iron electrodes
(Initial concentration = 5 mg/L)

Initial pH	Voltage, (V)	T= 20 min	T= 40 min	T= 60 min
3	20	83.80	93.60	98.60
	30	96.40	98.80	99.60
	40	97.60	99.60	99.80
7	20	90.40	98.40	99.20
	30	97.40	99.20	99.80
	40	98.20	99.60	99.90
10	20	97.40	98.40	99.40
	30	97.80	99.40	99.80
	40	97.80	99.80	99.90

Table 2: Percent of cadmium removal during electrocoagulation process using iron electrodes (Initial concentration = 50 mg/L)

Initial pH	Voltage, (V)	T= 20 min	T= 40 min	T= 60 min
3	20	91.80	98.44	99.180
	30	93.90	99.28	99.400
	40	94.58	99.96	99.980
7	20	93.90	98.46	99.820
	30	95.34	99.32	99.940
	40	97.44	99.98	99.994
10	20	98.20	99.88	99.900
	30	99.92	99.96	99.980
	40	99.92	99.98	99.998

Table 3: Percent of cadmium removal during electrocoagulation process using iron electrodes (Initial concentration = 500 mg/L)

Initial pH	Voltage, (V)	T= 20 min	T= 40 min	T= 60 min
3	20	98.450	99.766	99.958
	30	98.570	99.840	99.978
	40	99.826	99.950	99.984
7	20	99.196	99.794	99.966
	30	99.380	99.880	99.988
	40	99.850	99.892	99.992
10	20	99.596	99.914	99.982
	30	99.798	99.964	99.986
	40	99.934	99.990	99.996

Table 4: Iron electrode consumption during electrocoagulation process (g/L)

Voltage (V)	Weight of consumed electrode (g) Initial Cadmium Concentration		
	5.0 mg/L	50.0 mg/L	500.0 mg/L
20	2.97	4.47	2.61
30	4.37	4.93	3.66
40	9.37	9.39	8.45

Table 5: Energy consumption during electrocoagulation process (kw/kg), using iron electrodes, at voltage = 40V

pH	Energy consumption (kw/kg) initial cadmium concentration		
	5.0 mg/L	50.0 mg/L	500.0 mg/L
3	23.4	2.71	0.32
7	29.52	2.83	0.36
10	23.84	2.37	0.35

DISCUSSION

In the present study, electrocoagulation process has been evaluated as a treatment technology for cadmium removal from industrial effluents. Cadmium removal efficiency at different condition (pH, electrical potential) in various times was evaluated. It has been established in previous studies (Vik *et al*., 1984; Chen *et al*., 2000) that pH has a considerable effect on the efficiency of the electrocoagulation process. Also, as observed by other investigators the pH of the medium changed during the process. This change depends on the type of electrode material and initial pH.

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 cadmium. Removal efficiencies of cadmium as a function of initial pH with iron electrodes are presented in tables 1-3. As observed by other investigators (Vik *et al*., 1984), a pH increase occurs when the initial pH is low(< 7). Vik (Vik *et al*., 1984) ascribed this increase to hydrogen evolution at cathodes. However, this was contested by Chen (Chen *et al*., 2000), who 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. In addition, if the initial pH is acidic, reactions would shift towards which causes 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 and suggests that electrocoagulation can act as pH buffer. In this research, the influent pH did not affect the removal efficiencies significantly over a wide range. Therefore, pH adjustment before treatment is not required in practical applications. The highest efficiency of cadmium removal observed in alkaline medium (pH=10). The pH variation of solution after electrocoagulation process in various voltages showed that the final pH for all of experiments with iron electrodes is higher than initial pH, which is in agreement with results obtained later (Kobya *et al*., 2003). Preliminary laboratory testing of the electrolysis cell involved determining the effect of applied voltage on the efficiency of cadmium 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 (Letterman *et al.*, 1999; Holt *et al.*, 2002), which can influence the treatment efficiency of the electrocoagulation. Therefore, the effect of current density or electrical potential (voltage) on the pollutants removal was investigated. As expected, it appears that for a given time, the removal efficiency increased significantly with increase of current density. The highest electrical potential (40V) produced the quickest treatment with >99% cadmium reduction occurring after only 20 min and the lowest cadmium removal efficiency occurred in the lowest electrical potential (20V). This is ascribed to the fact that at high current, the amount of iron oxidized increased, resulting in a greater amount of precipitate for the removal of pollutants. In addition, it was demonstrated that bubbles density increases and their size decreases with increasing current density (Khosla *et al.*, 1991), 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 behavior is explained by the fact that the treatment efficiency was mainly affected by charge loading ($Q = It$), as reported by Chen (Chen *et al.*, 2000). 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 40V as an optimal electrical potential for the treatment of effluents containing cadmium, since it ensures the quickest removal rate with the lowest cost. A set of experiments was performed with different initial concentrations of cadmium to determine the time required for removal under various conditions of electrocoagulation process. The results obtained at different electrical potential showed that initial concentration of cadmium can effect on efficiency removal and for higher concentration of cadmium, higher electrical potential or more reaction time is needed. On the other hand, if the initial concentration increases, the time required of process should increase too. And, also it is clear from Tables (1-3) that in the higher the

concentration, the greater the time needed for removal of cadmium, but that higher initial concentrations of cadmium were reduced significantly in relatively less time than lower concentrations. The time taken for reduction thus increases slowly with increases 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 (Chaudhary *et al.*, 2003). The method was found to be highly efficient and relatively fast compared to conventional existing techniques and also, it can be concluded that the EC process has the potential to be utilized for the cost-effective removal of heavy metals from water and wastewater. The time dependence of cadmium removal by electrocoagulation process at different pH is shown in Tables 1-3. It can be seen from the tables that up to 83-99 % of the initial concentration decreased within 20 min of the process at different concentrations and the residual cadmium concentration in effluent were less 1.0 mg/L and finally at the end of reaction time (60 min) reached to < 0.003 mg/L, which is the recent guideline value of WHO (WHO, 2003) so we can discharged treated effluents to environment, in safety. At the beginning of process the cadmium removal is rapid and later it decreased gradually over almost the entire process examined. Cadmium ions are more abundant at the beginning of the electrocoagulation process, and the generated iron hydroxides due to corrosion of the anode at that time will form complexes with cadmium and therefore rapid removal of cadmium was observed. A set of experiments was performed with different initial concentrations of chromium (5, 50 and 500 mg/L) to examine the effect of the presence of organic matter (such as COD with concentration 100, 500 and 1000 mg/L O_2) and various levels of turbidity (10, 50 and 200 NTU) in wastewater on the removal efficiency of chromium. The results obtained at optimum conditions (pH=10, reaction time =60 min and voltage = 40V) showed that the removal efficiency for various concentrations of chromium was unchanged and hence the electrocoagulation

process can be applied efficiently for chromium removal in presence of organic matter and turbidity. A series of tests were conducted with different concentrations of cadmium in the solution and the weight of the electrode consumed with respect to different voltage levels is given in Table 4. As shown in the Table, it can be concluded that the higher the applied voltage, the higher the weight of the electrode consumed. Also, higher initial cadmium concentrations in the solution result in higher electrode consumption weights. As the Table illustrates, the weight of electrode consumed at 40 volts is much higher that that at 20 volts. Also, an increase in initial cadmium concentration to 500 mg/L, does not result in an important increase in electrode consumption. However, at this concentration, coagulation has taken place and the high formation of the flocs has helped the complexation of cadmium and there was no need for much consumption of the electrode as at low initial chromium concentrations. Table 5 shows energy consumption results for the removal of one gram of cadmium at 40V, initial chromium concentrations of 5, 50 and 500 mg/L, and pH 3, 7 and 10. It can be concluded that the consumed energy decreased with increase in initial cadmium concentration, because the flocs formation will help the adsorption of the cadmium from the solution. Finally, it can be concluded that electrocoagulation method is a reliable, safety, efficient and cost-effective method for removal of cadmium from industrial effluents, especially designed for pH = 10 and voltage = 40V. On the other hand, in this study it was shown that electrocoagulation process using iron electrodes achieves a fast and effective reduction of cadmium (more than 99%) present in industrial effluents (such as plating baths wastewater). Indeed, the reported results show that electrocoagulation is faster and more effective process as compared to other methods alone. Nevertheless, further studies should be carried out to confirm the practical feasibility of this method for treating various wastewaters and with different condition.

ACKNOWLEDGMENTS

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