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Removal of Cadmium from Industrial Effluents by Electrocoagulation Process Using Aluminum Electrodes

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Abstract: The object of this study is evaluation of cadmium removal from industrial wastewater by electrocoagulation process. For this study a glass tank in 1.56 liter volume with four plate electrode was used to do experiments. The electrodes made of aluminum 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^{-1} and then it was started up. The amount 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, Sludge Volume Index (SVI) 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 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 (40 V) 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.

Key words: Electrocoagulation process · cadmium · aluminum 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 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 [1]. 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 [2, 3].

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 conversion of ferrihydrite to goethite and hematite has been reported previously [4, 5]. The drinking water guideline value recommended by World Health Organization (WHO) is 0.005 mg Cd l^{-1} [6].

A variety of specialized treatment processes for the removal of heavy metals prior to their discharge into the environment have been developed [7]. Among them, the simple process of metals as insoluble hydroxides, carbonates, or sulfides is used in about 75% of electroplating facilities to treat wastewater [8].

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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 [8, 9].

Another way for cadmium removal from industrial wastewater is electrocoagulation process which is without any chemical material using and only uses transferring aluminum 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.

An examination of the chemical reactions occurring in the electrocoagulation process shows that the main reactions occurring at the electrodes are:

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

$$3H_2O + 3e \leftrightarrow {}^3/_2H_2 + 3OH^- \text{ (cathode)} \quad (2)$$

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

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

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:

$$2Cl^- \leftrightarrow Cl_2 + 2e \quad (4)$$

$$2H_2O \leftrightarrow O_2 + 4H^+ + 4e \quad (5)$$

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

$$Cl_2 + H_2O \leftrightarrow HClO + H^+ + Cl^- \quad (6)$$

$$HclO \leftrightarrow ClO^- + H^+ \quad (7)$$

The aluminum hydroxide flocs act as adsorbents and/or traps for metal ions and so eliminate them from the solution [10, 11]. Simultaneously, the hydroxyl ions which are produced at the cathode, increase the pH in the electrolyte and may induce coprecipitation of Cd in the form of their corresponding hydroxides [12, 13]. This acts synergistically to remove pollutants from water.

The goal of this research was to survey of efficiency of electrocoagulation process to removal of Cadmium from plating bath wastewater and was to determination of the effects of voltage, pH and reaction time on the removal efficiency.

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. 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^{-1}, 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 (1 M).

Experiments were performed in a bipolar batch reactor (Fig. 1), with four aluminum 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 10×13×12 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 was 10×10 cm. The distance between of electrodes was 1.5 cm, respectively. A power supply pack having an input of 220 V and variable output of 0-40 V with maximum current of 5 ampere was used as a direct current source.

The temperature of each system was maintained at 25±1°C. 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 min and then immediately filtered through a 0.45 μm mixed cellulose acetate membrane. The residual cadmium concentration was determined using Atomic Absorption method

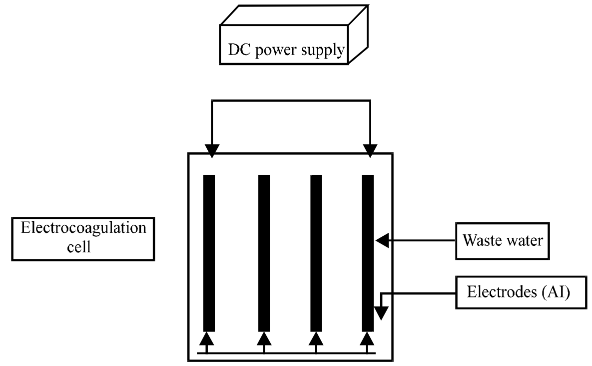

Fig. 1: A schematic diagram of the experimental set up

according to the standard method [14]. The amount of cadmium ion removal was measured at pH 3, 7 and 10 and in electrical potential of 20, 30 and 40 V. Also at the end of each stage of experiment, Sludge Volume Index (SVI) was measured.

RESULTS AND DISCUSSION

In the present study, electrocoagulation process has been evaluated as a treatment technology for cadmium removal from plating baths wastewater. Cadmium removal efficiency at different condition (pH, electrical potential) in various times was evaluated. It has been established in previous studies [13, 15] 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 are presented in Tables 1-3. As observed by other investigators [13], a pH increase occurs when the initial pH is low (<7). Vik *et al.* [13] ascribed this increase to hydrogen evolution at cathodes. However, this was contested by Chen *et al.* [15], who explained this increase by the release of CO_2 from wastewater owing to H_2 bubble disturbance.

Table 1: Percent of cadmium removal during electrocoagulation process (Initial concentration = 5 mg l^{-1})

pH	Voltage (V)	T= 20 min	T= 40 min	T= 60 min	SVI (mg l^{-1})
3	20	98.80	99.20	99.60	144.05
	30	99.00	99.40	99.80	80.35
	40	99.60	99.80	99.90	84.93
7	20	98.80	99.40	99.60	99.40
	30	98.80	99.60	99.80	81.95
	40	99.40	99.60	99.80	53.95
10	20	99.40	99.80	99.80	175.56
	30	99.60	99.80	99.80	20.51
	40	99.60	99.80	99.98	61.41

Table 2: Percent of cadmium removal during electrocoagulation process (Initial concentration = 50 mg l^{-1})

pH	Voltage (V)	T= 20 min	T= 40 min	T= 60 min	SVI (mg l^{-1})
3	20	94.20	98.30	99.72	75.46
	30	95.92	99.54	99.78	102.84
	40	99.38	99.68	99.84	51.01
7	20	96.00	96.92	99.70	267.03
	30	99.84	99.90	99.96	114.29
	40	99.92	99.98	99.98	59.73
10	20	99.72	99.84	99.90	195.65
	30	99.78	99.92	99.96	41.73
	40	99.94	99.98	99.98	66.39

Table 3: Percent of cadmium removal during electrocoagulation process (Initial concentration = 500 mg l^{-1})

pH	Voltage, (V)	T= 20 min	T= 40 min	T= 60 min	SVI (mg l^{-1})
3	20	98.310	99.582	99.776	937.00
	30	98.166	99.746	99.946	78.50
	40	99.812	99.924	99.964	63.86
7	20	98.738	99.636	99.854	408.76
	30	99.316	99.786	99.982	89.73
	40	99.794	99.926	99.986	54.90
10	20	99.348	99.872	99.964	92.20
	30	99.654	99.954	99.988	106.02
	40	99.914	99.978	99.994	63.15

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. As illustrated in Tables 1-3, 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 illustrated in Tables 4-6. As seen, the final pH for pH 3 and 7 of

Table 4: Changes of pH during electrocoagulation process for cadmium removal (initial concentration = 5 mg l^{-1})

Initial pH	Voltage (V)	Final pH
3	20	8.0
	30	9.3
	40	9.8
7	20	8.5
	30	10.1
	40	10.0
10	20	8.7
	30	8.9
	40	9.0

Table 5: Changes of pH during electrocoagulation process for cadmium removal (initial concentration = 50 mg l^{-1})

Initial pH	Voltage (V)	Final pH
3	20	8.6
	30	9.2
	40	9.3
7	20	9.7
	30	10.1
	40	10.0
10	20	9.2
	30	9.1
	40	9.1

Table 6: Changes of pH during electrocoagulation process for cadmium removal (initial concentration = 500 mg l^{-1})

Initial pH	Voltage (V)	Final pH
3	20	8.8
	30	9.1
	40	9.2
7	20	9.6
	30	9.3
	40	9.2
10	20	8.9
	30	9.1
	40	9.1

experiments is higher than initial pH, which is in agreement with results obtained later, but for initial pH (pH=10), the final pH was lower than 10 [16].

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 current not only determines the coagulant dosage rate but also the bubble production rate and size and the flocs growth [17, 18], 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 (40 V) 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 (20 V). This is ascribed to the fact that at high current, the amount of aluminum 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 [19], 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 [15]. 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 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 [20].

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 94-99% 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^{-1} and finally at the end of reaction time (60 min) reached to <0.05 mg l^{-1}, which is the recent guideline value of WHO [2] 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 aluminum hydroxides due to corrosion of the anode at that time will formcomplexes with cadmium and therefore rapid removal of cadmium was observed.

A set of experiments was performed with different initial concentrations of cadmium (5, 50 and 500 mg l^{-1}) to examination the effect of organic matter presence (such as COD with concentration 100, 500 and 1000 mg l^{-1}) in wastewater on removal efficiency of cadmium. The results obtained at optimum condition (pH=10, reaction time=60 min and voltage =40 V) showed that removal efficiency for various concentrations of cadmium was unchanged and hence electrocoagulation process can be apply efficiently for cadmium removal in presence of organic matter.

Also, in order to study the effect of turbidity (10, 50 and 200 NTU) on removal efficiency of cadmium a set of experiments was performed with different initial concentrations of cadmium (5, 50 and 500 mg l^{-1}). The results obtained at optimum condition (pH=10, time reaction = 60 min and voltage = 40 V) showed that the removal efficiency for various concentrations of cadmium was fairly fixed unchanged and hence electrocoagulation process can be apply efficiently for cadmium removal in presence of turbidity.

With regard to a series of tests conducted with different concentration of cadmium in the solution, the weight of the electrode consumed with respect to different voltage of the pilot under study is given in Table 7. As it is shown in the table, 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 concentration of the cadmium in the solution, the higher consumption of the electrode is resulted. As the Table represents the electrode consumed with 40 volts in the process is much more than the process conducted with 20 volts.

Table 7: Electrode consumption during electrocoagulation process (g l^{-1})

	Weight of electrode consumed (g)		
	Cadmium concentration (mg l^{-1})		
Voltage (V)	5.0	50.0	500.0
20	2.25	2.98	1.94
30	2.62	3.39	2.04
40	5.92	6.89	4.98

Table 8: Energy consumption during electrocoagulation process (kwh g^{-1}), at voltage = 40 V

	Energy consumed (kwh g^{-1})		
	Cadmium concentration (mg l^{-1})		
pH	5.0	50.0	500.0
3	15.12	1.92	0.29
7	28.92	2.76	0.33
10	23.34	2.29	0.30

Also, since the cadmium concentration in the solution has increased to 500 mg l^{-1}, the consumption of the electrode has not increased as much, but the coagulation has taken place, because the high formation of the flocs has helped and a boarded the cadmium and there was no need for much consumption of the electrode as before.

The SVI is a good parameter for determination of sludge settleability, which for suitable condition is around 50 to 150 mg l^{-1}. At present study, SVI for various conditions measured that showed in Tables 1-3.

The result of this study was showed (Table 8) that consumed energy for removal of one gram cadmium at electrical potential 40 V, initial concentration of cadmium 5 mg l^{-1} and pH 3, 7 and 10 was 15.12, 28.92 and 23.34 kwh, respectively and consumed enery for removal of one gram cadmium at electrical potential 40 V, initial concentration of cadmium 50 mg l^{-1} and pH 3, 7 and 10 was 1.92, 2.76 and 2.29 kwh, respectively. Also, with initial concentration of cadmium being 500 mg l^{-1}, pH of 3, 7 and 10 at electrical potential of 40 V, the energy consumed for removal of one gram of cadmium was 0.29, 0.33 and 0.30 kwh, respectively. It can be concluded that the consumed energy decrease with increase in 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 = 40 v. On the other hand, in this study it was shown that electrocoagulation process 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.

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