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Study on Removal of Cadmium from Plating Baths Wastewater by Electrochemical Precipitation Method

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Abstract: The object of this study is evaluation of cadmium removal from industrial wastewater by electrochemical precipitation method. This study is a Laboratory experimental study which was done in pilot plant form. A glass tank in 1.45 L volume with four plate electrode was used to do experiments. The electrodes made of aluminum and zinc and connect to the positive and negative pole of DC power supply, respectively (monopolar mode). The tank was filled with synthetic wastewater that was containing cadmium ion in concentration 50 and 250 mg L⁻¹ and then it was started up. The amount of cadmium ion removal was measured at pH 4, 6 and 10 and in electric potential range of 10 to 25 volts. When the initial concentration of cadmium ion was 50 mg L⁻¹, the highest amount of cadmium removal was 40 min after starting the process and when the initial concentration was 250 mg L⁻¹, the highest amount of removal was obtained 70 min after starting at 10, 20 and 25 volts. Efficiency of this process was more than 99%. The results show that in pH range from 4 to 10, this process is applicable. In initial stages of the process, with initial pH of 4 to 6, pH has increased but in initial pH of 10, in both concentrations pH has decreased. In the initial concentration 50 and 250 mg L⁻¹ of cadmium, SVI was 33.4-129.9 and 72.1-292.9 min. In electrochemical precipitation, the initial concentration was effective, so if the initial concentration increases, the time of process should increase too. In this process, the use of different electrical potentials can provide a wide range of pH for doing this process.

Key words: Electrochemical precipitation, cadmium, plating baths wastewater

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 (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 *et al.*, 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 conversion of ferrihydrite to goethite and hematite has been reported previously (Lin *et al.*, 2003; Sun *et al.*, 1996). The drinking water guideline value recommended by World Health Organization (WHO) is 0.005 mg Cd/L (Butter *et al.*, 1998).

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 precipitation 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 precipitation 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 (Karthikeyan *et al.*, 1996; Patterson, 1985).

Another way for cadmium removal from industrial wastewater is electrochemical precipitation method which is without any chemical material using and only uses transferring cadmium 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 a recent study Bartolozzi *et al.* (1995) carried out a study about hydrometallurgical recovery process for nickel-cadmium spent batteries. The efficiency of cadmium recovery was about 99% and energy consumption was found to be 2.2 kWh kg Cd. Also, Dziewinski *et al.* (1998) investigated electrochemical methods to process radioactive and hazardous (mixed) wastes at a bench scale. Cadmium, copper, mercury and chromium salts, cyanides and simple organic compounds were used in the tests. The goal of this research was to survey of efficiency of electrochemical precipitation process to removal of Cadmium from plating bath wastewater and was to determination of the effects of voltage, reaction time and pH on the removal efficiency.

MATERIALS AND METHODS

This study has been conducted in the environmental chemistry laboratory of School of Public Health of Isfahan University of Medical sciences in late 2005. All chemicals including cadmium sulfate, sodium hydroxide pellets, concentrated sulfuric acid and sodium chloride were used as received. Desired concentrations of Cd solution were

prepared by mixing proper amount of cadmium sulfate with deionized water. In order to increase the electrical 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 1:5 (volume) sulfuric acid solution and sodium hydroxide (0.2 M).

The electrochemical precipitation apparatus consists of a DC power supply, flat-plate anode and cathode (10×10 cm) mounted in a glass cell (1450 mL). There were two anodes and two cathodes according to the electrodes arrangement connected in a monopolar mode. Two electrodes were made of zinc and two electrodes were made of aluminum. The net spacing between the electrodes was 15 mm and the net volume of the reactor was about 1.14 l.

The pH values in influent and reactor unit were measured using a pH electrode and a Benchtop pH/ISI meter model 420A (Orion, USA), respectively. A Jenway Conductivity Meter (Model 4200) was employed to determine the conductivity of the solution. Calibration was made using the conductivity standard of 1413 mS cm⁻¹ (Jencons, USA) before each set of measurements. Finally, at the end of reaction the concentration of Cadmium in the reactor was analyzed by Atomic Absorption method according to the standard method (APHA *et al.*, 1992). The tank was filled with synthetic wastewater that was containing cadmium ion in concentration 50 and 250 mg L⁻¹ and then it was started up. Samples were taken after 20, 40 and 70 min. The amount of cadmium ion removal was measured at pH 4, 6 and 10 and in electrical potential of 10, 20 and 25 volts. At the end of each stage of experiment, Sludge Volume Index (SVI) was measured.

RESULTS

In the present study, electrical precipitation 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. The amount of cadmium ion removal for different condition was measured that showed in Table 1 and 2 for two initial concentration of cadmium (50 and 250 mg L⁻¹). Also, the SVI parameter of produced sludge during reaction was determined that present in Table 1 and 2.

The SVI is a good parameter for determination sludge settleability, which for suitable condition is around 50 to 150 mL g⁻¹. At present study, SVI for various conditions measured that showed in Table 1 and 2.

Table 1: Percent of cadmium removal during electrochemical precipitation (initial concentration = 50 mg L⁻¹)

SVI (mL g ⁻¹)	70 min	40 min	20 min	Voltage	pH
243	99.58	93.60	77.16	10	4
180	99.22	99.84	99.20	20	
33.6	86.80	99.90	99.54	25	
203	98.40	99.70	97.80	10	6
187.5	99.70	99.80	99.50	20	
57	99.70	98.50	99.30	25	
193.5	99.30	99.40	99.40	10	10
78.5	99.10	99.30	99.50	20	
129.9	99.70	99.90	99.70	25	

Table 2: Percent of cadmium removal during electrochemical precipitation (initial concentration = 250 mg L⁻¹)

SVI (mL g ⁻¹)	70 min	40 min	20 min	Voltage	pH
197	99.2	91.2	83.0	10	4
158	99.5	99.8	98.2	20	
190	99.9	99.8	96.4	25	
168.6	99.7	99.6	86.3	10	6
123.4	99.9	99.7	98.9	20	
77.4	99.9	99.6	99.9	25	
292.9	99.9	99.7	99.9	10	10
178.8	99.9	99.8	99.9	20	
72.1	99.9	99.9	99.9	25	

Table 3: Changes of pH during electrochemical precipitation process for cadmium removal (initial concentration = 50 mg L⁻¹)

70 min	20 min	Voltage	pH
8.2	7.1	10	4
8.7	8.3	20	
8.9	9.1	25	
8.1	8.1	10	6
8.8	8.9	20	
9.1	8.1	25	
8.8	9.0	10	10
9.1	9.3	20	
9.3	9.1	25	

Table 4: Changes of pH during electrochemical precipitation process for cadmium removal (initial concentration = 250 mg L⁻¹)

70 min	20 min	Voltage	pH
7.0	6.5	10	4
8.1	7.7	20	
7.4	7.1	25	
7.3	7.1	10	6
8.1	7.2	20	
7.2	9.1	25	
9.1	8.9	10	10
9.5	9.5	20	
9.4	9.6	25	

In the Table 3 and 4, changes of pH during electrochemical precipitation process showed.

The results of this study was showed that consumed energy for removal of one gram cadmium at electrical potential 25 v, initial concentration of cadmium 50 mg L⁻¹ and pH 4 and 10, is 28.53 and 13.01 Wh (Watt-hour), respectively. Also, consumed energy for removal of one gram cadmium at electrical potential 25 v, initial concentration of cadmium 250 mg L⁻¹ and pH 6 and 10, is 13.4 and 13.3 Wh (Watt-hour), respectively.

DISCUSSION

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 (Holt *et al.*, 2002; Letterman *et al.*, 1999), which can influence the treatment efficiency of the electrochemical precipitation. 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 Cadmium removal efficiency increased significantly with increase of current density.

The results of this study illustrated that the highest electrical potential (25 v) produced the quickest treatment with 99% cadmium reduction occurring after only 40 to 70 min and the lowest Cadmium removal efficiency occurred in the lowest electrical potential (10 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 (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 *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 25v as an optimal electrical potential for the treatment of effluents containing cadmium, since it ensures the quickest removal rate with the lowest cost.

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 of process should increase too.

The time dependence of cadmium removal by electrochemical precipitation process at different pH is shown in Table 1 and 2. It can be seen from the tables that up to 77-99.9 % of the initial concentration decreased within 20 min of the process and the residual cadmium concentration in effluent were less than 0.2 mg L⁻¹ and

finally at the end of reaction time (70 min) reached to 0.02 mg L^{-1} which is the recent guideline value of WHO (WHO, 1984), 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 electrochemical precipitation process and the generated aluminum hydroxides due to corrosion of the anode at that time will form complexes with cadmium and therefore rapid removal of cadmium was observed.

In electrocoagulation or electrochemical precipitation, a slight increase in the pH was observed with time during the process and it was within the regulatory drinking water standards. Vik *et al.* (1984) observed the same effect during the EC process and also reported that electrochemical process can act as pH neutralization step. The pH increase in electrocoagulation or electrochemical process is attributed to the formation of hydrogen gas at the cathode. Therefore, the effluent pH after electrochemical precipitation treatment would increase for acidic influent but decrease for alkaline influent that this is one of the advantages of this process (Vik *et al.*, 1984; Chen *et al.*, 2000). To examine the effect of influent pH on the electrochemical precipitation process, the synthetic wastewater was adjusted to the desired pHs (4, 6 and 10) for each experiment, using sulfuric acid and sodium hydroxide.

As observed by other investigators (Vik *et al.*, 1984; Chen *et al.*, 2000), the treatment induced an increase in the pH when the initial pH was low (Table 3 and 4). This might be explained by the excess of hydroxyl ions produced at the cathode in sufficiently acidic conditions and by the liberation of OH^- due to the occurrence of a partial exchange of Cl^- with OH^- in $\text{Al}(\text{OH})_3$ (Chen *et al.*, 2000). When the initial pH is high (about 10), the formation of $\text{Al}(\text{OH})_4^-$ species together with parasite attack of the cathode by hydroxyl ions (Picard *et al.*, 2000) lead to a slight decrease in the pH.

As illustrated in Table 1 and 2, 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.

Finally, it can be concluded that electrochemical precipitation method is a reliable, safety, efficient and cost-effective method for removal of cadmium from plating baths wastewater. On the other hand, in this study it was shown that electrochemical precipitation achieves a fast and effective reduction of cadmium (more than 99%) present in plating baths wastewater. The optimum value

of electrical potential, allowing fast removal (70 min) of cadmium with low electrode consumption, was found to be 28.53 and 13.01 Wh at pH 4 and 10 (and initial concentration = 50 mg L^{-1}), respectively. In addition, it was demonstrated that the naturally occurring pH of plating batch wastewaters is appropriate to achieve an effective treatment. Moreover, the final pH of treated effluent was nearly neutral which allows it to be directly discharged in natural aquatic streams. Consequently, electrochemical precipitation can be considered as a suitable alternative to existing methods. Indeed, the reported results show that electrical precipitation 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 industrial wastewaters and with different condition.

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