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Effects of operational parameters on cadmium removal from aqueous solutions by electrochemical coagulation

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ABSTRACT

The aim of present study is to investigate the feasibility of cadmium removal from water using electrocoagulation. Electrocoagulation (EC) is an electrochemical wastewater treatment technology with increased popularity and considerable technical improvements. In the study, effects of operating parameters such as initial solution pH, initial concentration (C_0), reaction time (t), stirring speed, and conductivity (κ) on cadmium removal from synthetic wastewater-containing cadmium in the batch electrocoagulation process were investigated. It was found from experimental results that initial solution pH is important parameter affecting cadmium removal. pH of initial solution was in the range of 3 to 6 in the experiments. The largest cadmium removal efficiency was obtained with pH 6. pH 6, obtained from initial solution whose pH was 6, reached an agreement with activity to pH diagrams for Al^{+3} species in equilibrium with $Al(OH)_3$. Although specific energy consumption increased with decreasing cadmium concentration, whose conductivity was low, cadmium removal efficiency was higher at $25\,mg\,L^{-1}$ than $1{,}000\,mg\,L^{-1}$. Stirring speed, below and above 150 rpm, reduces cadmium removal efficiency. The results showed that electrocoagulation method had high effectiveness in removing cadmium from aqueous solutions.

Keywords: Electrocoagulation; Cadmium removal; Aluminum electrode; pH; Treatment

1. Introduction

Heavy metals are among the main sources of environmental pollution. Cadmium (Cd), like other heavy metals, is released into natural waters by industrial and domestic wastewater discharges. Cd as a toxic heavy metal, which is found in industrial discharges of different industries such as manufacturing of cadmium–nickel batteries, phosphate fertilizers, pigments, stabilizers, alloys, and electroplating industries, has very harmful environmental impacts [1,2]. In addition, cadmium exists naturally as a minor constituent of base metal ores and coal deposits. As a result, it exists in effluent of related industries, e.g. zinc hydrometallurgical processes. There is no known function of cadmium in the human biological system. The presence of such foreign metal ion in human is likely to be a result of various exposures. In addition to direct exposure from air and drinking water, another potential exposure result from crops grown in the contaminated water and soil environment, which transports the metal into food

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chain where cadmium is accumulated in various parts of crops [3].

Methods proposed for Cd removal from wastewaters are those employed for most heavy metals, including ion exchange resins [4–6], solvent extraction [7,8], ultrafiltration [9], membrane technologies [10–12], precipitation [13–15], adsorption [16–20], electrochemical treatment [21–23], and biosorption [24–26]. Chemical precipitation is the most common conventional method of treatment for Cd-containing effluents [27]; however, large amount of sludge is produced during the treatment poses disposal problems. The other methods, although usually effective, are not free of drawbacks, high capital cost with recurring expenses and capability to treat only small volumes, are the most common. Economical, practical, and efficient alternative techniques are, therefore, required to treat Cd-containing wastewaters [28].

Electrocoagulation (EC) is an electrochemical wastewater treatment technology with increased popularity and considerable technical improvements. EC is a complicated process involving many chemical and physical phenomena using consumable electrodes to supply ions into the wastewater stream. In an EC process, coagulating ions are produced *"in situ"* and it involves three successive stages: (i) formation of coagulants by electrolytic oxidation of the "sacrificial electrode", (ii) destabilization of the contaminants, particulate suspension, and breaking of emulsions, and (iii) aggregation of the destabilized phases to form flocks [29].

EC has been successfully employed in removing metals, suspended particles, clay minerals, organic dyes, and oil and greases from a variety of industrial effluents. In this process, a potential is applied to the metal anodes, typically fabricated from either iron or aluminum, which causes two separate reactions: Fe/Al is dissolved from the anode generating corresponding metal ions, which almost immediately hydrolyze to polymeric iron or aluminum hydroxide. These polymeric hydroxides are excellent coagulating agents. The consumable (sacrificial) metal anodes are used to produce polymeric hydroxides continuously in the vicinity of the anode. Coagulation occurs when these metal cations combine with the negative particles carried toward the anode by electrophoretic motion. Contaminants present in the wastewater stream are treated either by chemical reactions and precipitation or physical and chemical attachment to colloidal materials being generated by the electrode erosion. They are then removed by electroflotation, or sedimentation and filtration. Thus, rather than adding coagulating chemicals as in conventional coagulation process, these coagulating agents are generated *in situ* [29].

Water is also electrolyzed in a parallel reaction, producing small bubbles of oxygen at the anode and hydrogen at the cathode. These bubbles attract the flocculated particles and, through natural buoyancy, float the flocculated pollutants to the surface.

When a potential is applied from an external power source, the anode material undergoes oxidation, while the cathode will be subjected to reduction or reductive deposition of elemental metals. The electrochemical reactions with metal M as anode may be summarized as follows:

- At the anode:

$$M_{(s)} \rightarrow M^{+n}_{(aq)} + ne^- \tag{1}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{2}$$

- At the cathode:

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)} \tag{3}$$

$$2H_2O_l + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \tag{4}$$

If aluminum electrodes are used, the generated $Al_{(aq)}{}^{3+}$ ions will immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. For example, Al^{3+} ions on hydrolysis may generate $Al(H_2O)_6{}^{3+}$, $Al(H_2O)_5OH^{2+}$, $Al(H_2O)_4(OH)^{2+}$, and the hydrolysis products may form many monomeric and polymeric species such as $Al(OH)^{2+}$, $Al(OH)^{2+}$, $Al_2(OH)_2{}^{4+}$, $Al(OH)^{4-}$, $Al_6(OH)_{15}{}^{3+}$, $Al_7(OH)_{17}{}^{4+}$, $Al_8(OH)_{20}{}^{4+}$, $Al_{13}O_4(OH)_{24}{}^{7+}$, $Al_{13}(OH)_{34}{}^{5+}$ over a wide pH range [30]. These hydroxides/polyhydroxides/polyhydroxymetallic compounds have strong affinity for dispersed particles as well as counter ions to cause coagulation. The gases evolved at the electrodes may impinge on and cause flotation of the coagulated materials.

In this study, experiments were conducted to examine the effects of the operating parameters such as initial solution pH, initial cadmium concentration (C_0), retention time (t), and conductivity (κ) on cadmium removal from simulated model of wastewater-containing cadmium in the batch EC process.

2. Materials and methods section

The experimental setup is schematically shown in Fig. 1. The EC unit consists of five pair of electrodes made of plate aluminum with total area of approximately 1,000 cm^2 and the gap between the electrodes is 5 mm. Electrodes were connected to a digital dc

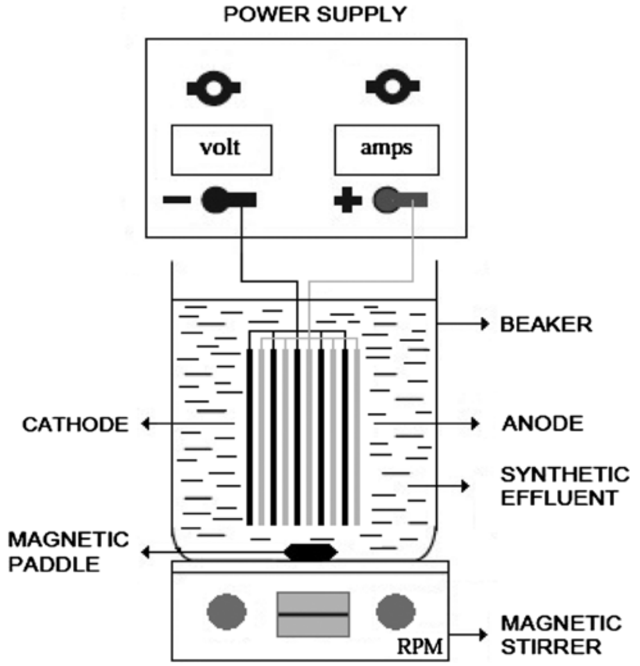

Fig. 1. Schematic diagram of an electrochemical reactor system.

power supply (Good-Will 3060 D) in monopolar mode. Two digital multimeters (Brymen Bm 201) as ampermeter and voltmeter were used to measure the current passing through the circuit and the applied potential, respectively. The EC unit has been stirred by a magnetic stirrer (Heidolp MR 3004 S). The thermostat electrocoagulator is made of plexiglass with the volume of 1,000 mL. During the experiments, temperature, conductivity, and pH of the wastewaters were measured by a multiparameter (WTW Multiline P-4 F-Set-3). Treated wastewater was collected over a desired period of time from the reactor and collected samples were filtered by the cellulose acetate membrane filter with the pore diameter of 0.45 μm (Schleicher and Schuell) before the analysis. Reactor was operated in batch and galvanostatic mode. Wastewater samples used in the experiments were prepared synthetically using $CdCl_2.H_2O$ having 99.99 of purity from Merck. The solution with cadmium concentration of 250 mg/L was prepared by dissolving 447.94 mg $CdCl_2.H_2O$ dried at 105˚C in distilled water and made up to 1 L with distilled water. pH adjustments were carried out by concentrated HNO_3 and NaOH (5 M); all chemicals used in the experiments are analytic grade from Merck. The analysis of cadmium was carried out using atomic absorption spectrometer (Shimadzu AA 6800, Japan) according to the Standard Methods for Examination of Water and Wastewater [31]. The parameters chosen in the experiments carried out were pH, cadmium concentration, current density, and stirring speed, whose ranges are given in Table 1.

Table 1
Experimental parameters

Parameters	Range
pH	3.0, 4.0, 5.0 and 6.0
Current density (mA/cm^2)	1.0
Cadmium concentration (mg/L)	25, 50, 100, 250, 500 and 1,000
Stirring speed (rpm)	50, 150 and 250

3. Results and discussion

3.1. Effect of initial pH and initial concentration on the removal efficiency

Based on preliminary experimental results, the effect of initial pH has been explored within the range of 3 and 6. The initial pH is one of the important factors in affecting the performance of electrochemical process. It has been established that the pH has a considerable influence on the performance of EC process. [32]. For investigating the effect of initial wastewater pH on the cadmium removal efficiency, experiments were performed at initial cadmium concentrations of 25, 50, 100, 250, 500, and 1,000 $mg\,L^{-1}$, current density of 1.0 $mA\,cm^{-2}$, stirring speed of 150 rpm, and solution temperature of 293 K. Metals precipitate in the form of metal hydroxides at high pH values. High pH values (higher than pH: 6) were excluded in order to prevent the deposition of metal hydroxide. Results are shown in Figs. 2 and 3.

As can be seen in Figs. 2 and 3, cadmium removal increased with increasing pH up to 6. Increasing cadmium removal had the same tendency for all cadmium concentrations at pH 6. For 250 $mg\,L^{-1}$ initial cadmium concentration, cadmium removal efficiency obtained using aluminum plate electrodes by EC are 77% for pH 3, 89% for pH 4, 95% for pH 5, and 98% for pH 6 at the end of 30 min. This tendency is in accordance with literature findings [33]. When the effect of initial pH on an EC system was investigated, distribution of aluminum hydrolysis product must be considered. The distribution of aluminum hydrolysis

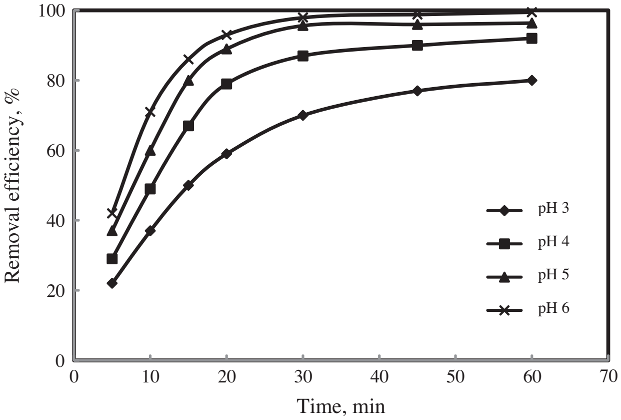

Fig. 2. The effect of initial pH on cadmium removal (initial cadmium concentration of 250 mg L^{-1}, stirring speed of 150 rpm, current density of 1.0 mA cm^{-2}, and solution temperature of 293 K).

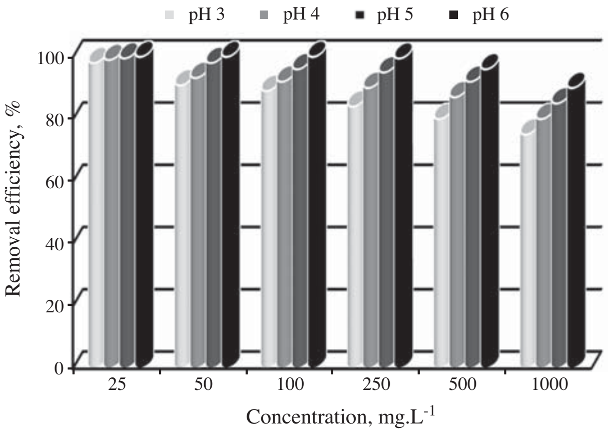

Fig. 3. The effect of initial pH on cadmium removal (initial cadmium concentration of all, stirring speed of 150 rpm, current density of 1.0 mA cm^{-2}, and solution temperature of 293 K).

product changes depending on solution pH. Amorphous $Al(OH)_3$ has the minimum solubility within the pH range from 6.5 to 7.8 [34]. Owing to the availability of efficient-coagulant in the medium and minimum solubility of the aluminum hydrolysis products in this pH range, it has been concluded that the highest removal rates are achievable. Fig. 4 shows that initial solution pH values increased during reaction time. As can be seen in Fig. 4, initial pH values increased during reaction time for all pH intervals investigated.

According to Fig. 4, it was determined that nearly no increase was seen in initial pH values of the solution during the first 10 min of the reaction in all pH ranges. pH values increased to 3.15, 4.21, 5.31, and 6.39 during the first 10 min for the initial pH values of 3, 4, 5, and 6, respectively. When removal efficiency are considered, it can be found that cadmium removal rates are 37, 49, 60, and 71% at pH values of 3, 4, 5, and 6, respectively. When removal efficiency obtained during the whole reaction period and pH trends in the solution are evaluated together, it is seen that cadmium removal is caused by cathodice deposition in the first 10 min of the reaction at all pH ranges. In this time period, ionic cadmium in the solution is degraded to metallic cadmium on cathode surface in convenience with the equation below:

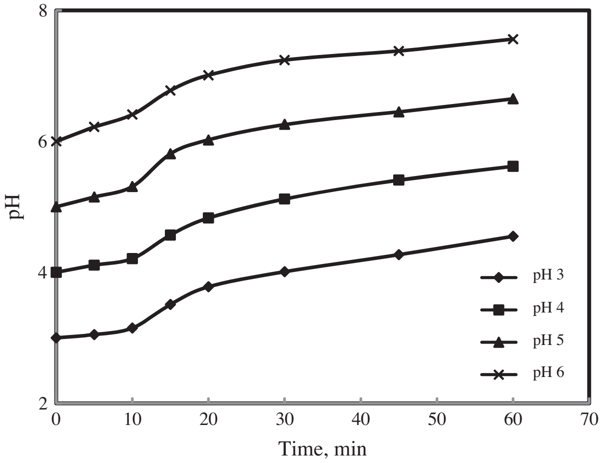

Fig. 4. The change of initial pH during reaction time (initial cadmium concentration of 250 mg L^{-1}, stirring speed of 150 rpm, current density of 1.0 mA cm^{-2}, and solution temperature of 293 K).

$$Cd^{2+}_{(aq)} + 2e^{-} \rightarrow Cd_{(s)} \tag{5}$$

It is an evidence for the presence of the cathode degradation in the process that pH range (6.5–7.8) required for the formation of amorphous $Al(OH)_3$, which has high-flocking capacity, at especially low pH values such as 3 and 4 was not reached at the beginning of the reaction and high removal efficiency was obtained at all pH ranges. This situation is also supported by the observation of the formation of flock in the reactor with the increasing pH values after the first 10 min of the reaction. In the later periods of the reaction, pH values increased in convenience with the reactions below;

$$2H_2O_l + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)} \tag{6}$$

$$2H_2O_l + O_{2(g)} + 4e^{-} \rightarrow 4OH^{-}_{(aq)} \tag{7}$$

As can be seen from Fig. 4, pH values at which the highest formation rate of amorphous $Al(OH)_3$ with high-flocking characteristics were obtained. In the experiments conducted with low pH values such as 3 and 4, pH values could not reach desired levels for the formation of amorphous $Al(OH)_3$ with high-flocking capacity and therefore it is thought that in these experiments EC process is not effective and cadmium removal is performed via cathode degradation dominantly.

Results showed that dominant removal mechanism in the cadmium removal using EC technique might change depending on the pH value of solution. Consequently, it can be stated that initial pH is an important parameter in electrochemical removal of cadmium and the highest cadmium removal rate was obtained with the initial pH of 6 in the present study. In addition, a cadmium removal rate of 99.5% was obtained with $1\,mA\,cm^{-2}$ current density, 150 rpm stirring speed, at a solution temperature of 293 K, $250\,mg\,L^{-1}$ initial cadmium concentration, and at the end of a 60 min reaction period.

The largest expense in electrochemical treatment processes is specific energy cost since no additional chemicals are needed. It is a requirement in electrochemical treatment and in the determination of optimum working conditions that the conditions where the best removal is performed as well as the lowest specific energy consumption is provided should be taken into consideration. In the present study, applied potential differences were measured using a voltmeter at all pH ranges. Specific energy consumption values were calculated according to Eq. (8) under constant current density.

$$W = \frac{I \times V \times t}{(C_0 \times V_0 - C_t \times Vt)} \tag{8}$$

where W is specific energy consumption ($kW\,h\,kg^{-1}$ Cd removed), I is current density (A), V is applied potential difference (V), t is reaction time (h), is initial Cd^{2+} concentration ($mg\,L^{-1}$), is volume of solution (L), is the concentration of Cd^{+2} at any given t time ($mg\,L^{-1}$). The most important factor determining the value of potential difference applied to the system under constant current density is specific electrical conductivity value. The pH of solution containing $250\,mg\,L^{-1}$ Cd^{2+} was about 5.75 and its conductivity was about $420\,\mu S\,cm^{-1}$.

Fig. 5 represents the specific conductivity values for the initial pH values of 3, 4, 5, and 6, respectively. As can be seen from the figure, as initial pH value decreases specific conductivity value increases. The lowest potential difference values due to the increase in conductivity value were obtained in the experiments where initial pH value was 3. At the end of the 60 min reaction time, specific energy consumption values were 17.9, 23.1, 25.7, and 28.1 ($kw\,h\,kg^{-1}$), for pH values of 3, 4, 5, and 6. Fig. 6 shows the specific energy consumption data obtained from the experiments.

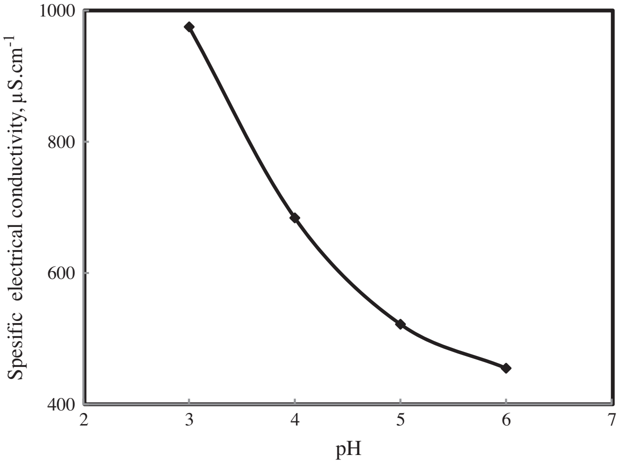

Fig. 5. Specific electrical conductivity vs. initial solution pH.

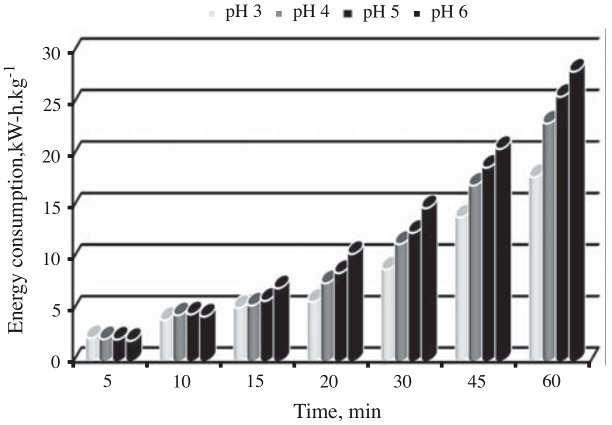

Fig. 6. The effect of initial pH on specific specific energy consumption ($250\,mg\,L^{-1}$ initial Cd^{2+} concentration, 150 rpm stirrer speed, and 293 K solution temperature).

When considered Fig. 6, it can be seen that specific energy consumption values are close to each other under constant current density since potential differences applied to the system are also close to each other for all pH ranges in the first 10 min period.

However, in the later periods of the reaction, differences in potential differences caused an increase in specific energy consumption with the increase in initial pH value.

At the end of the reaction time, when compared the conditions where initial pH values were from 3 and to 6, it was seen that specific energy consumption rate was 99.5% in the experiments where a rate of

80% Cd^{2+} removal was performed, which was 64% of the specific energy consumption rate of experiments where 99.5% removal was performed. This result is seen as a disadvantage for the conditions where initial pH value is 6 for the best Cd^{2+} removals.

When the effect of initial cadmium concentration on removal efficiency was investigated, the effect of initial cadmium concentration on specific energy consumption was calculated from obtained experimental results and is shown in Fig. 7.

As can be seen in Fig. 7, increased initial concentration caused a significant decrease in specific energy consumption. Solutions with high concentrations of cadmium have a much higher conductivity value from solutions with a low concentration of cadmium. High conductivity values have led to a lower potential difference in the electrochemical cell. According to Eq. (8), applied potential difference has led to fall to the low consumption of energy.

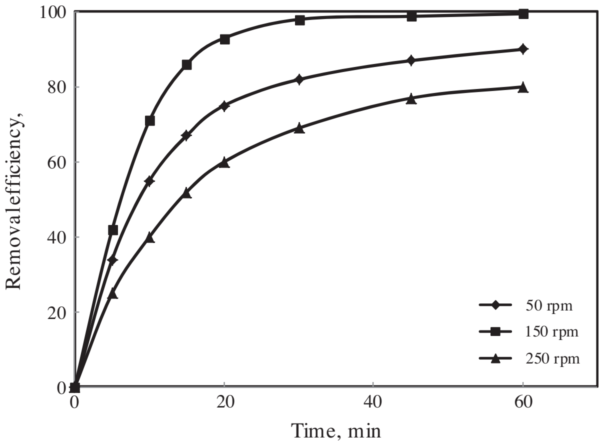

Fig. 8. The effect of stirring speed on cadmium removal (initial cadmium concentration of 250 mg L^{-1}, solution pH of 5.0, current density of 1.0 mA cm^{-2}, and solution temperature of 293 K).

3.2. The effect of stirring speed on cadmium removal

In the EC process, stirring speed applied to solution causes the increase of contact between the flocks and their agglomeration during the process. Heavy stirring speed can break the flocks, and amount of stirring speed must be optimized. The effect of stirring speed on the cadmium removal was examined with 50, 150, and 250 rpm of stirring speed. Current density of 1.0 mA cm^{-2} initial cadmium concentration of 250 mg L^{-1} and optimum pH of 5.0 were kept constant in the experiments. The supporting electrolyte was not used in the experiment. Increasing stirring speed decreased cadmium removal efficiency increasing stirring speed decreased capability of flock formation of aluminum ions. The stirring speed, smaller than 150 rpm, decreased cadmium removal efficiency and this speed did not supply a homogeneous mixture in the reactor. The results obtained are shown graphically in Fig. 8 for 250 mg L^{-1} initial cadmium concentration. Previous studies also investigated the effect of stirring speed and similar results were obtained with the results of this study [35].

The specific energy consumption values were calculated and are shown in Fig. 9. The specific energy consumption values increased contrary to the cadmium removal efficiency both for the stirring speed

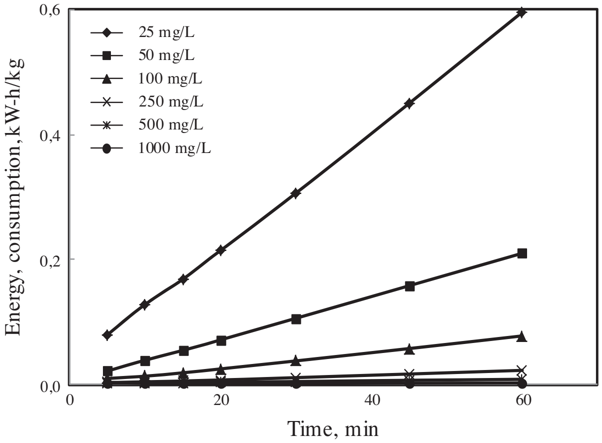

Fig. 7. The effect of initial cadmium concentration on specific energy consumption (stirring speed of 150 rpm, solution pH of 6.0, current density of 1.0 mA cm^{-2}, and solution temperature of 293 K).

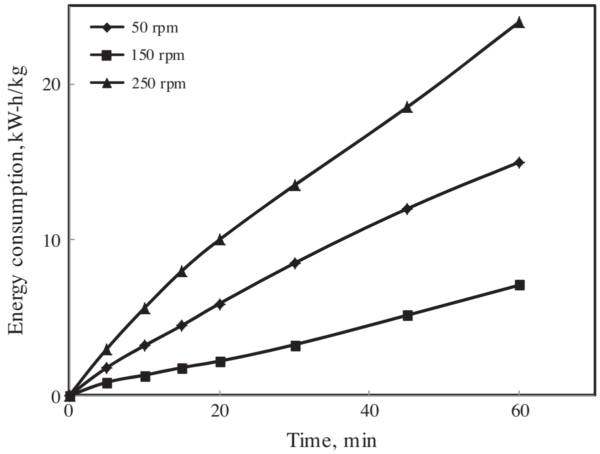

Fig. 9. The effect of stirring speed on specific energy consumption (initial cadmium concentration of 250 mg L^{-1}, solution pH of 6.0, current density of 1.0 mA cm^{-2}, and solution temperature of 293 K).

above 150 rpm (250 rpm) and below 150 rpm (50 rpm). Graphical results showed that it deposited between electrodes because of the electrochemical dissolution of aluminum could not mix homogeneously and this deposition caused increment of cell resistance at lower stirring speed. The increase in the cell resistance causes the increase of potential value in the systems where constant current density and this causes the increase of the amount of specific energy consumption per unit volume. It was considered that, the reason for higher specific energy consumption due to higher stirring speed is a result of high speed in the reactor creating negative pressure on the flow of electrons, which slows down the flow of electrons or creates an additional resistance. The stirring speed of 50 and 250 rpm were not preferred in terms of specific energy consumption. So the best stirring speed was 150 rpm for cadmium removal.

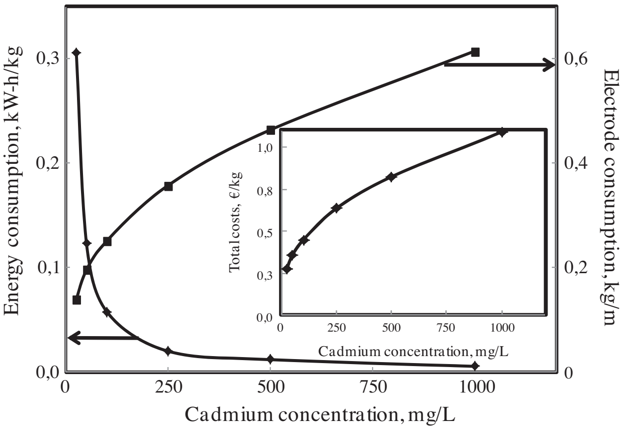

Fig. 10. Cost for the treatment synthetic solution containing different concentration of cadmium. Current density: 1.0 mA cm^2, pH: 6, stirring speed of 150 rpm.

3.3. Operation cost

In any electrochemical process, the main elements affecting operating cost are specific energy consumption and the cost of electrode material. The costs of these two are more important than other factors such as labor, maintenance, sludge disposal, and fixed costs. The costs of energy and electrode material have been taken into account as major cost items in the calculation of the operating cost.

$$\text{Operation Cost} = a\times C_{\text{energy}} + b\times C_{\text{electrode}} \qquad (9)$$

where C_{energy} (kWh/kg of removed cadmium) and $C_{\text{electrode}}$ (kg Al/m^3 of cadmium solution) are consumption quantities for the cadmium removal, which are obtained experimentally. "*a*" and "*b*" given for Turkish market in June 2011, are as follows: "*a*" electrical energy price 0.0838 €/kWh; "*b*" electrode material price 1.776 €/kg Al. Electrical specific energy consumption was calculated as Eq. (8). Electrode consumption (kg Al/m^3 cadmium solution) was calculated by the following equation by Faraday's Law:

$$C_{\text{electrode}} = \frac{M\times I\times t}{z\times F\times V} \qquad (10)$$

where I is current (A), t is time of electrolysis (s), M is molecular mass of aluminum (26.98 g/mol), z is number of electron transferred ($z = 3$), F is Faraday's constant (96,487 C/mol), and v is volume (m^3) of cadmium solution [36].

Operating costs for different initial cadmium concentration were calculated for the removal of cadmium from solutions with 25–1,000 mg/L initial cadmium concentration. The results are shown in Fig. 10. The results in Fig. 10 are a function time of removal efficiency. It can be stated from Fig. 10 that increasing initial concentration caused a decrease in specific energy consumption. In contrast to specific energy consumption, electrode consumption increased with increasing initial cadmium concentration because the time required achieving 100% removal efficiency increased for solutions with high initial concentration. The lowest operating costs for 25 mg/L cadmium concentration was 0.2739 €/kg at 25 min and the highest operating costs for 1,000 mg/L cadmium concentration was 1.0931 €/kg at 105 min.

4. Conclusion

Following results were obtained from the experimental data;

(1) The way of finding Al^{+3} ions given to the system electrochemically should be taken into consideration in the evaluation of the effect of the pH value in Cd^{2+} involving solution. Since the formation of $Al(OH)_3$ desired along the reaction period was not performed efficiently at low pH values such as 3 and 4, Cd^{2+} removal efficiency at high initial pH values (5–6) was higher in the present study. The best removal efficiency was 98% at pH 6.0.

(2) As can be seen from Fig. 3, effects of initial pH value of solutions involving various Cd^{2+} concentrations on Cd^{2+} removals by EC process showed the same trend.

(3) Because the specific conductivity value showed differences at different initial pH values, poten-

tial difference applied to the system in the experiments conducted under pH values with high specific conductivity value was low, and therefore, specific energy consumption was also lower. For the present study, specific energy consumption values increased from pH 3 to 6.

(4) This study showed that a removal rate of 99.5% could be performed in the solutions involving 250 mg L^{-1} of Cd^{2+} in the experiments where initial pH value was 6. It can be accepted that EC process is an effective process for the removal of Cd^{2+} even though specific energy consumption was high at this pH value when environmental importance of Cd^{2+} pollution is taken into consideration. Obtained of the experimental results are convenient according to Istanbul Water and Sewerage Administration.

(5) Stirring speed was very important for EC process because it provided a homogeneous distribution in the reactor. Low stirring rate was observed in the regional precipitation in reactor. Formation of flock slowed down at high stirring rate due to centrifugal force. The highest removal efficiency was obtained at 150 rpm because of the reasons mentioned above.

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