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Removal of sulfate by electrocoagulation with discontinuous electrodes in a continuous system

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ABSTRACT

This study aimed to remove sulfate from water solution through electrocoagulation, using multiple electrodes in a continuous flow system. Moreover, the effect of important parameters, including scenarios for voltages applying to electrodes, flow rate, primary sulfate concentration, and pH on the sulfate removal process was evaluated. The experimental reactor was a rectangular box of 20 × 10 × 6, all in cm. The electrodes were plates of grade 1050 aluminum. The highest sulfate removal was 87% that occurred at a voltage of 30 V and 10 mL/min of flow rate (retention time = 135 min) at pH = 5.5, when the initial concentration of sulfate was 500 mg/L. The highest sulfate removal rate in non-uniform voltage configuration was observed in the arrangement of 10, 20, and 30 V (upstream, middle, and downstream, respectively) during 135 min for 10 mL/min flow rate. On the other hand, the economic assessment revealed that the lowest amount of electrical energy consumed for removal of one mg/g of sulfate occurs at a 10 V uniform voltage among the electrodes. The results showed that the electrocoagulation technique could successfully be applied to continuous flow systems to remove sulfate from aquatic environments.

Keywords: Electrocoagulation; Removal of sulfate; Continuous flow configuration; Aqueous solution

1. Introduction

One of the most important issues of the modern world is the pollution of the environment due to the discharge of industrial wastewater and mining activities, which can introduce undesirable toxic chemicals to water and soil [1,2]. One of these undesirable chemicals is sulfate, which is one of the main anions present in natural waters and wastewater [3–5]. Natural resources of sulfate in surface water and groundwater are chemical weathering processes and decomposition of sulfide and sulfate minerals [6,7]. Sulfate from human activities is mainly released from wastewater of pulp and paper industry, chemical fertilizers, plastics industry, and extracting coal from mine [3,4]. The presence of sulfate in water causes undesirable flavor and bitter taste of water. Water with high concentrations of sulfate (more than 500 mg/L) causes diarrhea and gastrointestinal disorders in humans [8,9]. Sulfate cannot be easily removed since it is highly soluble and relatively stable in water [10]. Therefore, various purification methods based on physical, chemical, and biological processes have been proposed to reduce the sulfate concentration in water. Generally, physicochemical and biological methods are employed to treat sulfate-containing wastewater. Physicochemical methods

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are effective; however, they are not widely used in the industry due to high cost, energy demand, and the requirement for a separate system and appropriate disposal of the solid phase [11]. Given the fact that the concentration of sulfate in water is an important parameter in the removal of sulfate, the selection of an appropriate removal process largely depends on this factor [12,13]. Generally, sulfate removal processes can be divided into three categories of using membrane, sedimentation, and biological processes. The process of using membrane consists of three techniques: reverse osmosis, dialysis, and nano-filtration. Moreover, the sedimentation process can be carried out in three ways: ion exchange, co-precipitation, and electrochemistry [14]. The majority of proposed methods involve some cons including the production of large volumes of sludge, high cost of implementation and operation, and the need for secondary treatment of wastewater [11].

The application of electrochemical methods is conventional in different industries. Today, this technique has attracted significant attention as one of the most important and applicable tools for separation and control of pollutants. Some benefits of electrochemistry include compatibility with the environment, safety, and the possibility of the complete elimination of pollution [14,15].

Electrocoagulation is among the electrochemical methods to remove metals and ions from wastewater. In this process, chemical changes occur due to the presence of electrons released to the solution based on the difference in electrical potential levels between electrodes [16,17]. The oxidation and reduction in electrical coagulation on anode and cathode electrodes cause the creation of hydrogen and hydroxide anions in cathode as well as oxygen and cations production in the anode [18]. In this process, the electrolytic oxidation of the sacrificial electrode at anode causes sludge production. Metal ions produced in the anode electrode (usually aluminum) react with the produced hydroxide ions in the cathode electrode, creating metal hydroxide [17,19]. Reactions of oxidation-reduction taking place in the processes are described as follows [20–22]:

$$M\left(\text{insoluble}\right) \leftrightarrow M^{+n}\left(\text{soluble}\right) + \text{ne}^{-} \quad (1)$$

$$4\text{OH}^{-} \leftrightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^{-} \quad (2)$$

$$M^{n+}\left(\text{soluble}\right) + \text{ne}^{-} \leftrightarrow M'\left(\text{insoluble}\right) \quad (3)$$

$$2\text{H}^{+} \leftrightarrow 2\text{e}^{-} + \text{H}_2 \quad (4)$$

M is metal ion and n is the valence of the metal in the anode.

Hydrolysis of polyvalent metal ions, absorption of hydrolyzed species for destabilizing of colloidal particles, accumulation of unstable particles through intercellular connection, accumulation of unstable particles by particle transport, and van der Waals forces, and deposition of metal hydroxides are the dominant mechanisms of electric coagulation process [23–25].

Several researchers studied the removal of sulfate from tap water with electrocoagulation. Fifty-two percent and Ninety-two percent of sulfate and arsenic in the continuous system was removed from Guanajuato mine sewage in Mexico with a single electrode [22]. Removal of sulfate from water contaminated by deposition of calcium sulfate in a batch system [24], nitrate, and sulfate removal from municipal wastewater using aluminum electrodes in a discontinuous system [26], simultaneous removal of sulfate, sulfide, and sulfite by electrical coagulation using three different electrodes of iron, aluminum, and titanium in a discontinuous system [6] are among those researches conducted in this field. This process has been widely in industrial wastewater treatment as well [27–29].

In the present study, sulfate removal by the system of multiple and discontinuous electrodes in a reactor with a continuous flow of contaminated water was evaluated on a laboratory scale. The evaluated parameters include pH of the solution, uniform and non-uniform voltages, flow rate, and primary concentration of the solution.

2. Materials and methods

2.1. Materials

This laboratory-scale study was conducted on a continuous flow configuration. Wastewater samples with initial sulfate concentrations of 1,000; 500; 250 mg/L were produced by dissolution of anhydrous sodium sulfate in distilled water. 0.1 M HCl and NaOH solutions were employed to adjust the pH of the solution. In addition, 0.02 N NaCI was applied to increase the electrical conductivity of the solution. All chemicals used in these tests were obtained from Merck Co., Germany (German Merck Company) and all of the tests were repeated for at least three times. Moreover, errors in measurement of voltage were less than 1%, flow rate less than 5%, weight less than 1%, and volume less than 5%.

The electrodes were prepared from commercially available aluminum sheets of Grade 1050.

2.2. Methods

2.2.1. Overall process of sulfate removal

The overall process of sulfate removal with electrocoagulation is shown in Fig. 1. Tests were performed in a continuous reactor with a size of 60 mm × 100 mm × 200 mm, where baffles of 50 mm × 60 mm × 16 mm (Fig. 2). Aluminum electrodes were a rectangular plate of 100 mm × 25 mm × 1 mm. All electrodes were rinsed with distilled water and hydrochloric acid before use. Moreover, the programmable power supply was employed (model: PST-3201/3202, made by GwINSTEK Co.) as a stable source of electricity. On the other hand, a peristaltic pump (made by Sina Lab Equipment Co., Tehran) was used to create a continuous flow of the solution in the reactor. Samples containing specific concentrations of sulfate, after the adjustment of pH, supplied into the reactor vessel by the peristaltic pump at flow rates of 10, 20, 30, and 40 mL/min. After applying the electrical currents with specific voltages, samples were obtained from the reactor's outlet. After the sedimentation period (30 min), samples were taken from the solution for further measurements. Then, the samples were passed through the membrane filter with an opening size of 0.45 μm. In the next

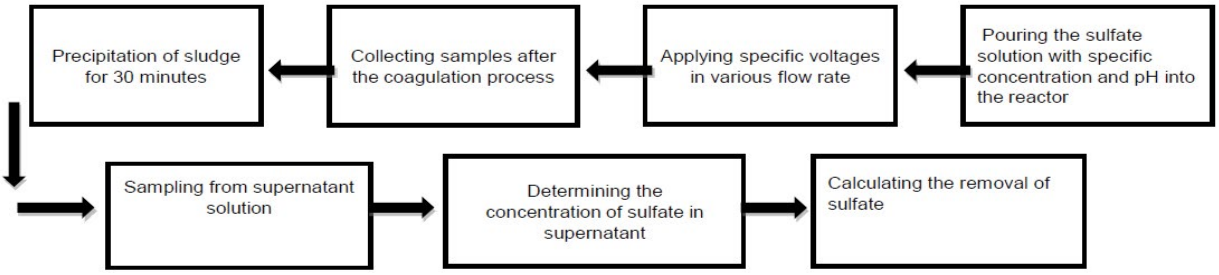

Fig. 1. Schematic of the experiment process.

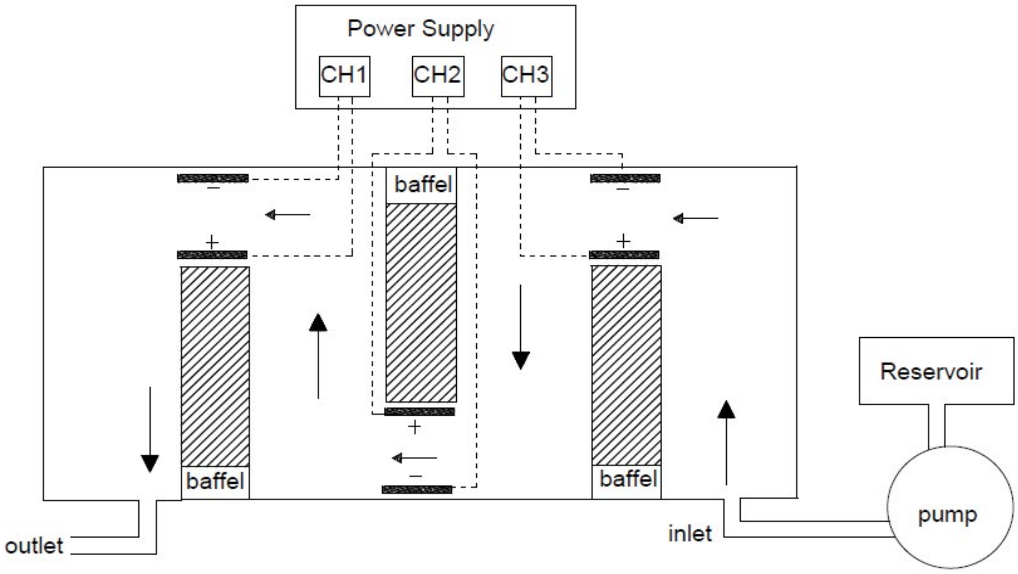

Fig. 2. Overall view of the reactor used in this study.

stage, spectrophotometry with a HACH DR6000 at 420 nm wavelength was performed to assess sulfate concentration.

Calculation of the sulfate removal and electrical consumption from the solution was performed using Eqs. (5) and (6). In those equations, C_0 and C_t indicate the initial and final concentration of sulfate in the solution respectively (mg/L), "W" is the electric power consumption (kWh), "V" for voltage (V), "I" for current (A), and "t" for time of operation (h).

$$\text{Removal}(\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \tag{5}$$

$$W = VIt \tag{6}$$

2.2.2. Evaluation of effective parameters on sulfate removal

In the present research, the effect of the following parameters in the removal of sulfate were evaluated:

- The effects of pH, 4.5, 5.5, and 6.5, on sulfate removal, were studied. Sulfate concentration in the primary solution and the voltage were set at 500 mg/L and 30 V, respectively.
- The effects of voltage, 10, 20, and 30 V, and current on the sulfate removal were assessed at the optimum pH obtained from the previous stage. The primary sulfate concentration was set to 500 mg/L.
- The role of solution concentration on the amount of sulfate removal was investigated for three concentrations of 350, 500, and 1,000 mg/L The optimum pH and voltage obtained earlier were applied.
- The impacts of applying a non-uniform voltage in electrodes with regard to a similar condition in uniform voltage state were studied. The impact of the arrangement of the discontinuous electrode with various values of voltage in electrodes of the reactor was assessed at this stage. To this end, different voltages were applied to each pair of electrodes. The applied voltages were as follows: $V = 10, 20, 30$; $V = 10, 30, 20$; $V = 20, 10, 30$; $V = 20, 30, 10$; $V = 30, 20, 10$; $V = 30, 10, 20$ (all in volts and from the inlet toward the outlet of the reactor).

2.2.3. Method for the analysis of the production of sludge and evaluating the effect of coagulation process on soluble temperature

To investigate the heat released by the electrocoagulation process, the temperature of the solution at the inlet and the outlet of the reactor was measured under optimal removal condition.

Also, according to the Eh-pH chart (Fig. 3), different types of dissolved aluminum at different pHs are shown as [30,31].

$$\mathrm{Al}_{(s)} \rightarrow \mathrm{Al}^{3+} + 3\mathrm{e}^- \tag{7}$$

$$\mathrm{Al}^{3+} + \mathrm{OH}^- \rightarrow \mathrm{Al}(\mathrm{OH})^{2+} \tag{8}$$

$$\mathrm{Al}(\mathrm{OH})^{2+} + \mathrm{OH}^- \rightarrow \mathrm{Al}(\mathrm{OH})^{+} \tag{9}$$

$$\mathrm{Al}(\mathrm{OH})_2^{+} + \mathrm{OH}^- \rightarrow \mathrm{Al}(\mathrm{OH})_3 \tag{10}$$

$$\mathrm{Al}(\mathrm{OH})_3 + \mathrm{OH}^- \rightarrow \mathrm{Al}(\mathrm{OH})_4^{-} \tag{11}$$

2.2.4. Economic evaluation method of coagulation process

Furthermore, the electrical energy consumed in various states of uniform and non-uniform voltages was measured to inspect the economy of the electrocoagulation process. On the other hand, the amount of consumed energy for removal of one mg/g of sulfate from the solution was calculated. This makes possible to compare the electrocoagulation configurations more comprehensive.

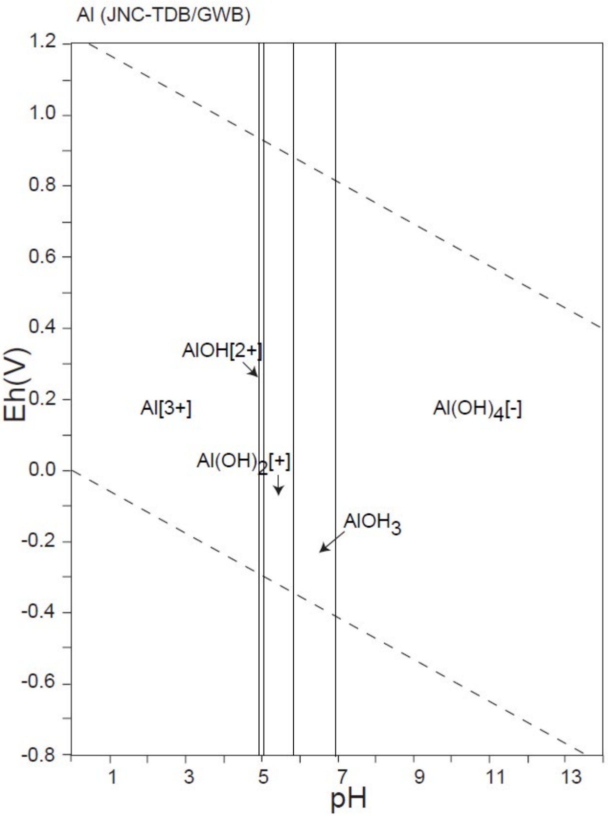

Fig. 3. Diagram pH-Eh [27].

3. Results and discussions

3.1. Effect of pH on sulfate removal

The role of pH on the removal of sulfate from the solution was evaluated. Three different pH levels (4.5, 5.5, and 6.5) in a solution of sulfate with a concentration of 500 mg/L were used. In addition, the tests of this stage were carried out at 30 V for flow rates of 10, 20, 30, and 40 mL/min. The results are illustrated in Fig. 4.

The voltage and flow rates were 30 V and 10 mL/min (retention time = 135 min), and the concentration of sulfate was 500 mg/L. The maximum sulfate removal were 62%, 87%, and 60% at pH of 4.5, 5.5, and 6.5, respectively. Under these conditions, the amount of residual sulfate in the solution after the coagulation process at pH 4.5, 5.5, 6.5 was 190, 65, and 200 mg/L, respectively. The results show that at pH 5.5, the highest sulfate removal efficiency was obtained from the solution, which is consistent with the results of the Bazrafshan et al. [32] research.

The removal process showed dependency to pH and flow rate as illustrated in Fig. 4. As flow rate increased from 10 to 40 mL/min, or retention time from 135 to 33 min, the removal drops from 87% to 40% at pH = 5.5.

The pH at the end of each test was measured to evaluate the mechanism of sulfate removal as shown in Fig. 5. pH was increased from 9 to 12 throughout the electrocoagulation and sulfate removal processes under all voltages and flow rates. In this regard, the maximum pH of the solution occurred for the case of 30 V and the flow rate of 10 mL/min where the highest sulfate removal (87%) occurred.

The elevation of pH might be due to the formation of hydroxide ions in the cathode electrode. Increased pH in the electrocoagulation process and reaction between aluminum and hydroxide ion occurred due to the mechanism of oxidation in the anode (1, 2) and reduction in the cathode (3, 4) [12,14,33]. Aluminum hydroxide is a hydrophobic hydroxide, therefore, pH is an important factor for the flocculation of aluminum hydroxide. In this regard, our findings are in agreement with the results obtained by other researchers, who assessed the simultaneous removal of sulfate and arsenic using the electrocoagulation process [14,19].

3.2. Effect of voltage on sulfate removal

In this stage, the optimal pH obtained in the previous phase (pH = 5.5) was used. Voltages of 10, 20, and 30 V applied on the flow rates of 10, 20, 30, and 40 mL/min. The results are shown in Fig. 5. As seen, the maximum removal were observed in flow rates of 10 and 20 mL/min at all three voltages. In shorter retention times, flow rates of 30 and 40 mL/min, the removal had a downward trend. According to the results, it could be stated that the voltage of 30 V and flow rate of 10 mL/min had the maximum removal efficiency, which is consistent with the results of the Bazrafsahn et al. [34] and Nouri et al. [35] research.

Therefore, the voltage of 30 V was selected as the optimal voltage at this stage. In fact, the results indicated that increasing voltage, increased the removal in a way that the removal of sulfate at the voltage of 30 V was 87%. In other

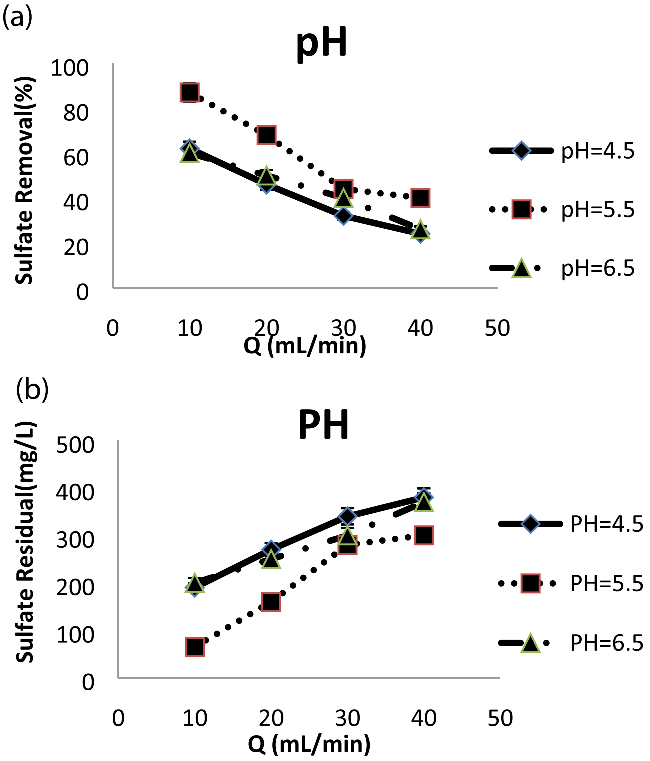

Fig. 4. Effects of pH changes on the removal of sulfate from wastewater, (a) sulfate removal percentage and (b) sulfate residual (voltage = 30 V, initial concentration of sulfate = 500 mg/L).

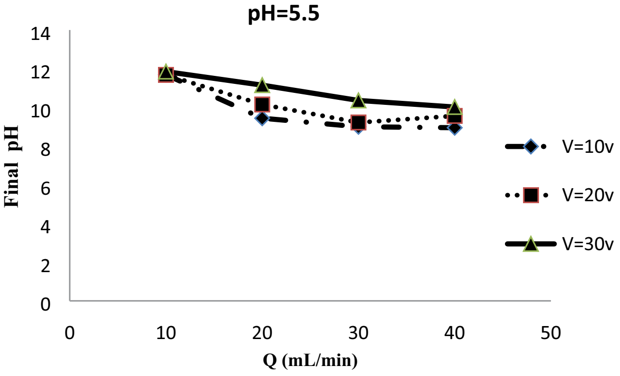

Fig. 5. Effect of electrocoagulation on pH of wastewater in initial pH levels and various values of voltage (voltage = 10, 20, 30 V, initial concentration = 500 mg/L).

words, higher voltages led to more release of aluminum hydroxide, resulting in coagulating more sulfate from the solution [36,37].

According to the results, an increment of voltage is from 10 to 30 V in flow rate of 10 mL/min in pH = 5.5, resulted in an increased sulfate removal rate from 66% to 87%. In addition, the sulfate removal rate increased from 40% to 87% in voltage value of 30 V in flow rates of 40 and 10 mL/min. The Faraday's Law may justify such an increase as in Eq. (12), where higher voltage value leads to greater release of aluminum hydroxide and an increase of coagulant. Moreover, high voltage value led to more formation of H_2 gas, which resulted in the increased collision of coagulants and increased contact surface [6,38]. In the end, the optimal voltage value was determined at 30 V at this stage.

$$W_A = i\times t\times m/n\times f \tag{12}$$

In Eq. (12), "W_A" is the weight of the dissolved anode (gr), "i" is flow intensity (A), "t" is exploitation time (s), "n" is the number of released electrons, "F" is Faraday constant, and "m" is the aluminum special molecular mass (g/mol).

3.3. Effect of the initial concentration of sulfate on sulfate removal

The initial concentration of sulfate, which was assessed at the final stage of optimization, affects the removal of sulfate from the solution. In this phase, the optimal pH of 5.5 and voltage of 30 V applied to the sulfate concentrations of 500, 250, and 1,000 mg/L with the flow rates of 10, 20, 30, and 40 mL/min. The results are presented in Figs. 6a and b. As observed, the primary sulfate concentration had an inverse impact on the sulfate removal rate. For instance, removal from a solution of high concentration sulfate (1,000 ppm) when the optimal reaction time (135 min in the flow rate of 10 mL/min) and voltage (30 V) were applied, was less than the removal of the lower concentrations under the same condition. This is an indication of the need for more Al^{3+} ions through higher voltage and retention time in a higher concentration of sulfate.

These results are in agreement with previous studies reportedly with higher removal rates at lower concentrations of pollutants using the electrocoagulation technique [39]. According to the results, the electrocoagulation process was able to remove 64% and 87% of the sulfate at the initial concentrations of 250 and 500 mg/L, respectively. It is noteworthy that the amount of remaining sulfate at the two mentioned concentrations was somehow similar and within the range of 65–90 mg/L (Fig. 7).

3.4. Effect of non-uniform voltage regulation in electrodes on the sulfate removal rate

This section presents the evaluation of the effect of non-uniform electrode arrangement with non-uniform voltage (different voltages in each electrode existing in the reactor). In the step, six various arrangements for 10, 20, 30 V in electrodes were assessed. However, the primary condition of both stages was considered equal (concentration of 500 mg/L and pH = 5.5) in order to be able to compare the results with results of uniform voltages. Results are presented in Fig. 8. Generally, there was an increase in the efficiency of sulfate removal by increasing the voltage of the electrodes downstream ward. At a flow rate of 10 mL/min, the sulfate removal efficiency reached to 70% in non-uniform voltage of V = 30, 20, 10 V while the reverse order of voltages, for example, V = 10, 20, 30 V, only removed 48% of sulfate.

Moreover, an increased flow rate from 10 to 40 mL/min in the voltage arrangement of V = 30, 20, 10 V led to decreased efficiency of sulfate removal from 70% to 37.4%.

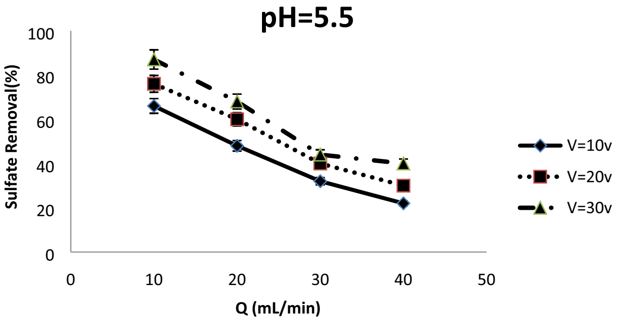

Fig. 6. Effects of voltage changes on the removal of sulfate from wastewater (pH = 5.5, initial concentration of sulfate = 500 mg/L).

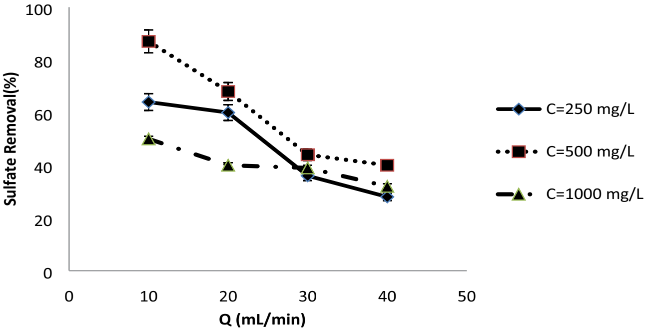

Fig. 7. Effects of initial concentration on the removal of sulfate from wastewater (voltage = 30 V, pH = 5.5).

This issue demonstrated the effect of retention time on establishing the coagulation process. In addition, results indicated that the level of sulfate removal from the discontinuous arrangement with non-uniform voltages of V = 30, 20, 10 V and V = 30, 10, 20 V was estimated at 70% and 62% where the remaining sulfate was 150 and 190 mg/L in these voltages, respectively (Fig. 8). Comparison of the sulfate removal using a uniform voltage of 30 V in all three electrodes (87% sulfate removal) with the application of non-uniform voltage of V = 30, 20, 10 V (70% sulfate removal) indicated that the use of the uniform voltage of 30 V in all electrodes increased the level of sulfate removal, however, the results should undergo a detailed economic analysis before coming to any conclusion.

3.5. Analysis of sludge produced during the coagulation process

The analysis of sludge production during the coagulation processes was carried out through six tests with uniform voltages of 20, 10, 30 V in flow rates of 10 and 30 mL/min and one test at a flow rate of 10 mL/min and non-uniform voltage (V = 30, 20, 10 from the entrance to exit of the reactor). Results obtained from the analysis of sludge produced during the mentioned tests are presented in Table 1. According to the results, the largest concentration of sludge was 450 mg/L that occurred at a flow rate of 10 mL/min and V = 30. In fact, the higher the voltage, and the longer retention time, the more efficient removal rate and the larger concentration of sludge in the coagulation process.

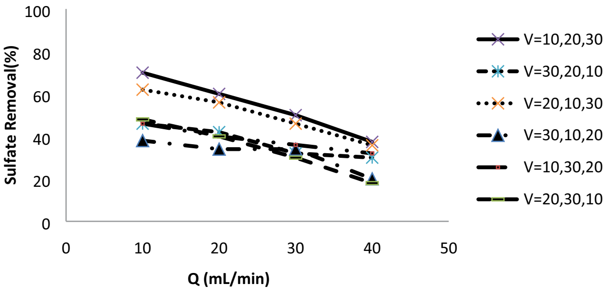

Fig. 8. Effect of non-uniform voltage in electrodes on the removal of sulfate (pH = 5.5, initial concentration of sulfate = 500 mg/L).

However, there was a lower level of sludge production (300 mL) in the test with non-uniform voltage with regard to the efficiency almost equal to the uniform voltage of 30 V (70%). Furthermore, the density of wet sludge in the coagulation process with a flow rate of 10 mL/min and uniform voltage of 30 V was equal to 0.33 (g/cm^3), which reduced to 0.18 (g/cm^3) due to reduction of voltage to 10 V. This is mainly due to the fact that the density of sludge is smaller, compared to water, which makes the sludge floating in the solution during the electrocoagulation process. Moreover, the aluminum existing in the sludge and solution was 402 (mg/L) and 26.56 (mg/L) at the voltage of 30 V and flow rate of 10 mL/min, respectively. Reduction of voltage to 10 V led to an increased level of aluminum (120 and 22.8 mg/L) in the sludge and solution, respectively. According to the results, the level of produced sludge and released aluminum in the solution and sludge was significantly lower in the equal flow rate of (10 mL/min) at the non-uniform voltage of V = 30, 20, 10 V, compared to the uniform voltage of 30 V. This shows one of the benefits of using a uniform voltage in electrodes.

3.6. Evaluation of temperature changes during electrocoagulation

In order to evaluate the process, temperature changes in the solution were evaluated at the end of the coagulation process at the flow rate of 10 mL/min and uniform voltages of 20, 30, 10 V in three electrodes and six modes of non-uniform voltages in electrodes. It is noteworthy that the temperature of the solution was equivalent to 20°C at the beginning of all tests. Results of the mentioned tests are presented in Table 2, which indicated that an increase of voltage from 10 to 30 V in electrodes resulted in an increased temperature of outlet solution from the reactor from 28°C to 54°C. According to previous results (Table 2), the increase of voltage led to higher removal efficiency. Therefore, one could conclude that the sulfate removal process by electrocoagulation is generally an exothermic process due to the occurrence of the electrolysis phenomenon in the reactor. Therefore, the temperature of the solution increases by improving the removal efficiency. It should be noted that the application of non-uniform voltages in electrodes led to the lower level of changes in the temperature of outlet solution in six tested models (Table 2), where the temperature was changed in the range of 37°C–38°C. This result can

Table 1
Analysis of sludge produced during the coagulation process (pH = 5.5, initial concentration of sulfate = 500 mg/L)

Soluble aluminum (mg/L)	Sludge aluminum (mg/kg)	Density of wet sludge (g/mL)	Volume of wet sludge (mL)	Total sample size (mL)	Test conditions	
					V (V)	*Q* (mg/L)
19.89	40	0.219	31.3	200	10	30
21.96	65	0.151	32.1	300	20	30
23	129	0.167	44.2	350	30	30
22.8	120	0.178	30	300	10	10
24.31	150	0.218	71.2	400	20	10
26.56	402	0.334	131.2	450	30	10
19.12	160	0.262	54.1	300	30, 20, 10	10

Table 2
Evaluation of temperature changes during electrocoagulation at different voltages (pH = 5.5, initial concentration of sulfate = 500 mg/L, flow rate = 10 mL/min, initial soluble temperature = 20°C)

Soluble temperature after the coagulation process (°C)	Voltage of electrodes (V)
28	*V* = 10
41	*V* = 20
54	*V* = 30
37	*V* = 10, 20, 30
35	*V* = 20, 10, 30
31	*V* = 10, 30, 20
28	*V* = 30, 10, 20
30	*V* = 30, 20, 10
33	*V* = 20, 30, 10

be an indication of another advantage of non-uniform voltage in electrocoagulation.

3.7. Evaluation of the amount of electrical energy consumed in the coagulation process

The amount of electrical energy consumed in uniform and non-uniform voltages was evaluated at pH = 5.5 and initial contaminant concentration of 500 mg/L (Fig. 9). According to the results, the increase of uniform voltage in electrodes from 10 to 30 V at flow rate of 10 mL/min led to increased consumption of electrical energy from 10.1 to 109.31 kWh. In the uniform voltage of 30 V, an increase of flow rate from 10 to 40 mL/min resulted in a decreased level of energy consumption from 109.31 to 33.5 kWh, respectively. However, no significant difference was observed in the amount of electrical energy consumed in non-uniform voltage in electrodes with various models in a constant flow rate. In addition, the increase of flow rate in both uniform and non-uniform voltage arrangements of electrodes in all models led to less electrical energy consumption in this process.

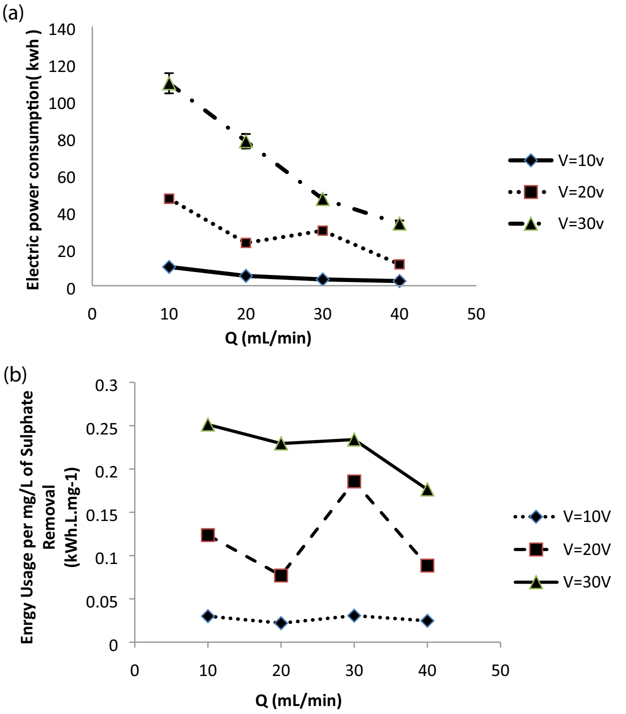

Fig. 9. Evaluation of the amount of electrical energy consumed in the coagulation process (a) electric power consumption, (b) energy usage per mg/L of sulfate removal (pH = 5.5, initial concentration of sulfate = 500 mg/L).

On the other hand, comparison of energy consumed in the uniform voltage of 30 V in electrodes (109.31 kWh) with non-uniform voltage of *V* = 10, 30, 20 V in electrodes (45.5 kWh) with level of sulfate removal of 87% and 70%, respectively, at the flow rate of 10 mL/min demonstrated an economic justification in use of the discontinuous electrode arrangement with non-uniform voltage with regard to high cost of electrical energy. In addition, a comparison of Figs. 10a and b indicate that generally, the increase of voltage was associated with a higher, but more expensive, sulfate removal rate from the solution. However, no specific flow rate can be economically prioritized. This comparison showed the importance of the discontinuous electrodes system since it is concluded that change in voltage, which is accompanied by changes in the current, requires less electrical energy. In terms of energy consumption per unit of removed concentration, it was observed that while the non-uniform arrangement had a suitable performance, energy consumption was just slightly above 0.05 kW for *t* the same decrease in concentration.

Studies in this research showed that in the continuous system using aluminum electrodes, in assessing the pH parameter, the removal rate of sulfate in the acidic pH range of 5.5 had the highest sulfate removal efficiency, which is consistent with the results of the research which is conducted by Mamelkina et al. [40] on the removal of sulfate electrocoagulation method and this research showed that in acidic pH 2 and 5, it had the highest rate of removal of sulfate. Also, with the results of Murugananthan et al. [6], the highest percentage of removal of sulfate, sulphide, and sulfite in pH is equivalent to 5.

Also in this study, the effect of uniform voltages and initial concentration of sulfate has been investigated. The results indicate that at a voltage of 30 V and flow rate of 10 mL/min the removal rate is equivalent to 87% which is consistent with the results of Dell Angel et al. [22] and Bazrafshan et al. [36]. The results in former one, in the removal of sulfate with alumina electrodes in a sample with a high voltage removal rate of 52% were observed, and also with the results of latter one, by increasing the voltage, the more removal efficiency observed in the removal of cadmium is perfectly consistent.

In evaluating the initial concentration of the solution, the results indicated that at a concentration of 1,000 ppm, with a retention time of 135 min (flow rate of 10 mL/min) and voltage of 30 V, the removal was 50%. This suggests that in higher concentrations of sulfate, the same level of sulfate removal requires more time. A similar conclusion was made by Bazrafshan et al. [36], which suggests that the removal of cadmium by electrical coagulation should be increased if the initial concentration increases, requiring more retention time for the removal process. This could be due to the need for more Al^{3+} ions in the higher concentrations of the sulfate.

In this study, the non-uniform voltage parameter was also investigated. Different voltages were applied to the electrodes and the results showed that with the voltage arrangement of $V = 30, 20, 10$ V, the removal of 70% was seen. This part was not reported in the literature to compare the results to this study.

In the economical aspect of the study, the evaluating of electrical energy consumption showed that in non-uniform voltages, the amount of electrical energy consumed was 45.5 kWh/h with the removal of 70% sulfate, and at a constant voltage of 30 V the electrical energy consumption was 109.31 kWh with the removal percentage of 87% sulfate. In fact, higher voltage will result in higher electrical energy consumption, consistent with the results of Ucar et al. [41] research in 2013. Therefore, due to the high price of electrical energy, the use of non-uniform voltage is more economical due to the optimal removal rate. In another word, non-uniform voltages are more suitable for sulfate removal in industrial scale [41].

In this study, the analysis of the production of sludge and the effect of temperature on a uniform and non-uniform voltages were investigated and the results showed that at the time of 135 min at non-uniform voltage, the amount of produced sludge and aluminum in the solution was lower than the uniform voltages. The highest amount of released alumina in the sludge section is from the electrocoagulation process, and this event has been the advantages of using non-uniform voltages.

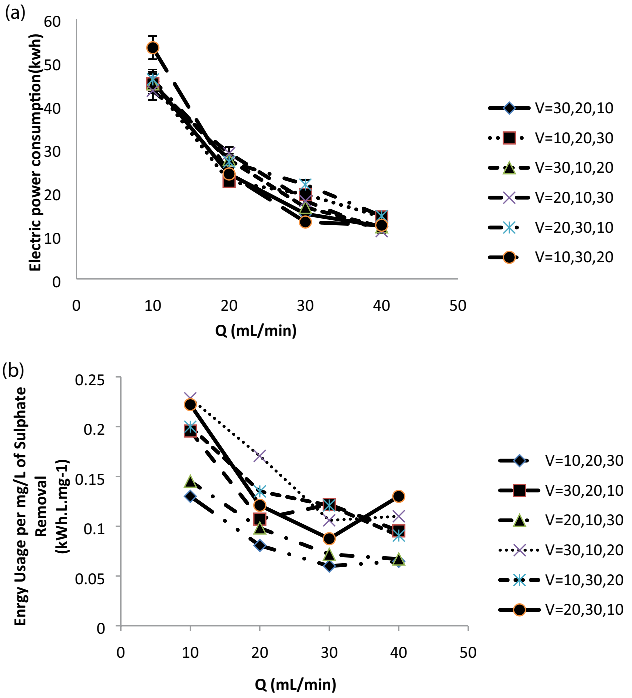

Fig. 10. Evaluation of the amount of electrical energy consumed in the coagulation process at non-uniform voltages (a) electric power consumption and (b) energy usage per mg/L of sulfate removal (pH = 5.5, initial concentration of sulfate = 500 mg/L).

Also in the evaluation of temperature variation due to increased removal efficiency at a uniform voltage of solution output temperature ranging from 40 to 54, but in non-uniform voltages, the solution temperature was within the range of 28° to 37°, which was not observed in the research.

4. Conclusion

In the current research, the effect of uniform and non-uniform voltages in discontinuous electrodes was evaluated in the electrocoagulation process to eliminate sulfate. In addition, the level of sulfate removal in uniform voltage at flow rates of (10, 20, 30, and 40 mL/min) and pH = 5.5 was assessed. According to the results, the highest percentage of sulfate removal was obtained at 87% in the uniform voltage of 30 V and flow rate of 10 mL/min. Furthermore, the results of uniform voltages were applied to evaluate the electrode arrangement with various voltages for each pair of the electrode. At this stage, the tests were carried out with six modes of voltage arrangement in electrodes. In general, the primary condition of the two stages was considered similar in order to compare the results obtained in this stage with the results of the stage of uniform voltages.

Results also demonstrated that the maximum elimination amount (70%) was observed in the non-uniform voltage of 10, 20, 30 V, and a discontinuous electrode arrangement at a flow rate of 10 mL/min from the entrance to existing of the reactor. Furthermore, the amount of electrical energy consumption was estimated in uniform and non-uniform voltages. According to the results, the amount of consumed electrical energy was 45.5 kWh in the non-uniform voltage. Meanwhile, energy consumption was 109.31 kWh in uniform voltage of 30 V and fa flow rate of 10 mL/min. With regard to the estimation of consumed electrical energy and the importance of this energy, in terms of evaluation of process efficiency, the discontinuous arrangement with non-uniform voltage was more economically justified. In general, the electrocoagulation process is an effective and favorable method to eliminate sulfate from water solution.

References

[1] K.S. Hashim, A. Shaw, R. Al Khaddar, M. Ortoneda Pedrola, D. Phipps, Iron removal, energy consumption and operating cost of electrocoagulation of drinking water using a new flow column reactor, J. Environ. Manage., 189 (2017) 98–108.

[2] K.S. Hashim, N.H. Al-Saati, S.S. Alquzweeni, S.L. Zubaidi, P. Kot, L. Kraidi, A.H. Hussein, R. Alkhaddar, A. Shaw, R. Alwash, Decolourization of dye solutions by electrocoagulation: an investigation of the effect of operational parameters, IOP Conf. Ser.: Mater. Sci. Eng., 584 (2019) 1–8, doi: 10.1088/1757-899X/584/1/012024.

[3] M. Ahmadi, F. Ghanbari, Optimizing COD removal from greywater by photoelectro-persulfate process using Box–Behnken design: assessment of effluent quality and electrical energy consumption, Environ. Sci. Pollut. Res. Int., 23 (2016) 19350–19361.

[4] A.J. Silva, M. Varesche, E. Foresti, M. Zaiat, Sulfate removal from industrial wastewater using a packed-bed anaerobic reactor, Process Biochem., 37 (2002) 927–935.

[5] X.J. Guo, Z.Y. Lu, P. Wang, H. Li, Z.Z. Huang, K.F. Lin, Y.D. Liu, Diversity and degradation mechanism of an anaerobic bacterial community treating phenolic wastewater with sulfate as an electron acceptor, Environ. Sci. Pollut. Res., 22 (2015) 16121–16132.

[6] M. Murugananthan, G.B. Raju, S. Prabhakar, Removal of sulfide, sulfate and sulfite ions by electrocoagulation, J. Hazard. Mater., 109 (2004) 37–44.

[7] S. Taita, W.P. Clarkeb, J. Kellera, D.J. Batstone, Removal of sulfate from high-strength wastewater by crystallization, Water Res., 43 (2009) 762–772.

[8] Y. Chen, Y. Wen, Q. Zhou, J. Huang, J. Vymazal, P. Kuschk, Sulfate removal and sulfur transformation in constructed wetlands: the roles of filling material and plant biomass, Water Res., 102 (2011) 572–581.

[9] WHO, Guidelines for Drinking Water Quality, World Health Organization, Geneva, 2011.

[10] M. Shams, M. Qasemi, M. Afsharnia, A.H. Mahvi, Sulphate removal from aqueous solutions by granular ferric hydroxide, Desal. Water Treat., 57 (2016) 23800–23807.

[11] L. Shan, Z. Zhang, Y. Yu, J. Ambuchi, Y. Feng, Performance of CSTR–EGSB–SBR system for treating sulfate-rich cellulosic ethanol wastewater and microbial community analysis, Environ. Sci. Pollut. Res. Int., 24 (2017) 14387–14395.

[12] F. Ntuli, T. Falayi, U. Thwanane, Removal of Sulphates from Acid Mine Drainage Using Desilicated Fly Ash Slag, In: International Conference on Waste Management and the Environment, V 202 ISSN 1743-351 (WM), 2016, doi: 10.2495/WM160341.

[13] S. Dill, J. Cowan, A. Wood, A removal of sulfate removal options from mine water, J. Int. Mine Water Assoc., 2 (2012) 329–342.

[14] Y.A. Mollah, R. Schennach, J.P. Parga, Cocke, Electrocoagulation (EC)-science and applications, J. Hazard. Mater., 84 (2001) 29–41.

[15] E.G. Filatova, Optimization of electrocoagulation technology of purifying wastewaters of ions of heavy metals, J. Water Chem. Technol., 38 (2016) 167–172.

[16] Q. Luo, T.K. Tsukamoto, K.L. Zamzow, Arsenic, selenium, and sulfate removal using an ethanol-enhanced sulfate-reducing bioreactor, Mine Water Environ., 27 (2008) 100–108.

[17] M. Zeppilli, M. Villano, F. Aulenta, S. Lampis, G. Vallini, M. Majone Effect of the anode feeding composition on the performance of a continuous-flow methane-producing microbial electrolysis cell, Environ. Sci. Pollut. Res. Int., 22 (2014) 7349–7360, doi: 10.1007/s11356–014–3158–3.

[18] I. Sirés, E. Brillas, M.A. Oturan, M.A. Rodrigo, M. Panizza, Electrochemical advanced oxidation processes: today and tomorrow: a review, Environ. Sci. Pollut. Res. Int., 21 (2014) 8336–8367.

[19] T. Sahu, B. Mazumdar, P.K. Chaudhari., Treatment of wastewater by electrocoagulation: a review, Environ. Sci. Pollut. Res. Int., 21 (2014) 2397–2413.

[20] D. Syam Babu, T.S. Anantha Singh, P.V. Nidheesh, M. Suresh Kumar, Industrial wastewater treatment by electrocoagulation process, Sep. Sci. Technol., 55 (2019), doi: 10.1080/01496395.2019.1671866.

[21] C.C. Jara, C.A. Martínez-Huitle, R.A. Torres-Palma, Distribution of nitrogen ions generated in the electrochemical oxidation of nitrogen containing organic compounds, Port. Electrochim. Acta, 27 (2009) 203–213.

[22] P. Dell Angel, G. Carreno, J.L. Nava, M.T. Martinez, J. Ortiz, Removal of arsenic and sulfates from an abandoned mine drainage by electrocoagulation, influence of hydrodynamic and current density, Int. J. Electrochem. Sci., 9 (2014) 710–719.

[23] D. Ghernaout, Electrocoagulation process for microalgal biotechnology -a review, Appl. Eng. Agric., 3 (2019) 85–94.

[24] J. Girczy, I. Kupich, Reduction of sulphate ions concentration in discharge waters from Zn-Pb mines, Physicochem. Probl. Miner. Process., 40 (2006) 125–134.

[25] K. Jüttnera, U. Gallab, H. Schmieder, Electrochemical approaches to environmental problems in the process industry, Electrochim. Acta, 45 (2009) 2575–2594.

[26] A.K. Sharma, A.K. Chopra, Removal of nitrate and sulphate from biologically treated municipal wastewater by electrocoagulation, Appl. Water Sci., 7 (2017) 1239–1246.

[27] E. Bazrafshan, M.H. Alipour, A.H. Mahvi, Textile wastewater treatment by application of combined chemical coagulation, electrocoagulation, and adsorption processes, Desal. Water Treat., 57 (2016) 9203–9215.

[28] E. Bazrafshan, F. Kord Mostafapour, M.M. Soori, A.H. Mahvi, Application of combined chemical coagulation and electrocoagulation process to carwash wastewater treatment, Fresenius Environ. Bull., 21 (2012) 2694–2701.

[29] A.H. Mahvi, S.J. Ebrahimi, A. Mesdaghinia, H. Gharibi, M.H. Sowlat, Performance evaluation of a continuous bipolar electrocoagulation/electrooxidation-electroflotation (ECEO-EF) reactor designed for simultaneous removal of ammonia and phosphate from wastewater effluent, J. Hazard. Mater., 192 (2011) 1267–1274.

[30] N. Takeno, Atlas of Eh-pH diagrams, National Institute of Advanced Industrial Science and Technology Research Center for Deep Geological Environments, Geological Survey of Japan, No. 419, 2005.

[31] F. Shen, X. Chen, P. Gao, G. Chen, Electrochemical removal of fluoride ions from industrial wastewater, Chem. Eng. Sci., 58 (2003) 987–993.

[32] E. Bazrafshan, A.H. Mahvi, S. Nasseri, M. Shaieghi, Performance evaluation of electrocoagulation process for diazinon removal from aqueous environments by using iron electrodes, Iran. J. Environ. Health Sci. Eng., 4 (2007) 127–132.

[33] K.W. Canton, Chapter 1: Fluid Waste Disposal, In: Treatment of Wastewater by Electrocoagulation Method and the Effect of Low Cost Supporting Electrolytes, Nova Science Publishers, Inc., New York, NY, 2010, pp. 1–49.

[34] E. Bazrafshan, K. Aldin Ownagh, A.H. Mahvi, Application of electrocoagulation process using iron and aluminum electrodes for fluoride removal from aqueous environment, J. Chem., 9 (2012) 2297–2308.

[35] J. Nouri, A.H. Mahvi, E. Bazrafshan, Application of electrocoagulation process in removal of zinc and copper from

aqueous solutions by aluminum electrodes, Int. J. Environ. Res., 4 (2010) 201–208.

[36] E. Bazrafshan, A.H. Mahvi, S. Nasseri, A.R. Mesdaghinia, F. Vaezi, Sh. Nazmara, Removal of cadmium from industrial effluents by electrocoagulation process using iron electrodes, Environ. Health. Sci. Eng., 3 (2006) 261–266.

[37] M. Nisha Priya, S. Esakku, K. Palanivelu, Electrochemical treatment of landfill leachate, J. Indian Chem. Eng., 47 (2005) 272–276.

[38] M. El. Amrety, M. Mossad, M. Fouad, Removal of Chlorpyrifos from aqueous solution using Electrocoagulation, Mansoura Eng. J., 43 (2018) 1–6.

[39] C. Jimenez, C. Saez, P. Canizares, M.A. Rodrigo, Optimization of a combined electrocoagulation - electroflotation reactor, Environ. Sci. Pollut. Res., 23 (2016) 9700–9711.

[40] M. Mamelkina, S. Cotillas, E. Lacasa, C. Sáez, R. Tuunila, M. Sillanpää, A. Häkkinen, M.A. Rodrigo, Removal of sulfate from mining waters by electrocoagulation, Sep. Purif. Technol., 182 (2017) 87–93.

[41] C. Ucar, M. Bilici Baskan, A. Pala, Arsenic removal from drinking water by electrocoagulation using iron electrodes, Korean J. Chem. Eng., 30 (2013) 1889–1895.