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Research Note

Drinking water softening with electrocoagulation process: Influence of direct and alternating currents as inductive with different arrangement rod electrodes and polarity inverter

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Abstract. This study investigates the process of electrocoagulation with direct and alternating currents as inductive using Fe and Al rods with different arrangements and a polarity inverter and based on the factors related to the efficacy of the process for drinking water softening. The efficacy of the electrocoagulation (EC) process was investigated in the batch mode under different conditions. Further, the amount of energy and electrode consumption and the amount of sludge produced were determined. Total hardness (98.26%) and calcium hardness (87.69%) were reduced with the highest efficiency using alternating current with Fe-Al electrode arrangement under optimal conditions (pH of 9, current density of 9 mA/cm^2, and electrolysis time of 12 min). Optimum charge loading was 0.54F/m^3. Maximum energy and electrode were consumed at the optimum current density using direct current, which were measured at 2.47 kWh/m^3 and 2.12 kg/m^3, respectively. Maximum sludge was produced at optimum current density using alternating current of 0.098 kg/m^3 with the settleability of 0.075 L/g and, also, using direct current of 0.109 kg/m^3 with the settleability of 0.063 L/g. This study showed that through the alternating current and using Fe electrodes, EC technology could be used as an alternative, new method for reducing water hardness with high efficiency and low energy consumption.

1. Introduction

1.1. Drinking water

Nowadays, drinking water resources are depleting at an alarming rate due to natural and artificial contamination and population growth. Aside from spring water, the water necessary for industries and household use is supplied from deep wells. Further to this,

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water treatment for drinking purposes is becoming more complicated because of more strict guidelines. One of the qualitative indexes of water, which is constantly monitored and is important for industrial purposes such as textile factories and cooling towers to produce high-quality products, is water hardness. The hardness of water is the result of polyvalent cations including calcium (Ca) and magnesium (Mg) [1]. Ca and Mg are non-organic chemical parts that can be found in significant amounts in water. Mg salts are more soluble than Ca salts and have laxative effects in high concentrations, but are less abundant in nature [2]. High water hardness causes many problems in both household and industrial settings such as sedimentation, blocking warm water pipes, boilers, water tabs, the equipment used in the piping systems of the membranes used in water treatment centers, kitchenware, and reaction with soap. Moreover, high water hardness causes disease contraction such as eczema and nephrosis [3]. Drinking water is classified based on their hardness to soft (0-50 mg/L), moderate (50-100 mg/L), hard (100-150 mg/L), and very hard (>150 mg/L) ratios. Water hardness ought to be less than what the drinking water guidelines have specified, i.e., 270 mg/L for Ca and 50 mg/L for Mg [4]. Removing water hardness to prevent the mentioned problems is called water softening. Among the processes used for softening water are reverse osmosis, electro-dialysis, ion exchange, chemical sedimentation, evaporation, crystallization, distillation, and membrane processes [5]. These technologies are subject to problems such as high sludge production, permanent increase in water hardness, increase in water salt such as Na, the costs of operation which are high per capita, and sedimentation on the membranes [6,7]. These disadvantages have prompted new-found demand for effective new technologies for softening water for industrial and drinking purposes [8].

1.2. Electrocoagulation process

The electrocoagulation (EC) process is one of the technologies that has attracted much attention for water and wastewater treatment in recent years. EC is the process of producing metal hydroxide flocks in water or wastewater through electrical analysis of soluble anodes made of iron (Fe) or aluminum (Al). In the anode, because of the electrochemical oxidation of Fe or Al, metal cations are produced, although they occur usually in the cathode hydrogen production. This process includes many physical and chemical reactions such as electrical discharge, anode oxidation, cathode reduction, coagulation, and absorption and constitutes three consecutive steps [9]:

a) *Coagulant production through the electronic oxidation of the sacrificial anode.* The main reaction that occurs in this stage is the analysis of the anode electrode made of Fe or Al:

$$Al_{(s)} \rightarrow Al^{3+} + 3e^{-},$$

$$4Fe_{(s)} \rightarrow 4Fe^{2+}_{(aq)} + 8e^{-}. \qquad (1)$$

Moreover, the electrolysis of water occurs at the cathode or anode:

Cathode reaction:

$$2H_2O + 2e^{-} \rightarrow H2_{(g)}2OH^{-}, \qquad (2)$$

Anode reaction:

$$2H_2O \rightarrow 4H^{+} + O_{2(g)} + 4e^{-}. \qquad (3)$$

b) *Destabilizing pollutants, suspending particles, and breaking emulsions.* In this step, a direct electrochemical reaction of metal cations on the surface of cathodes may occur:

$$Mn^{n+} + ne^{-} \rightarrow nMe^{0}. \qquad (4)$$

In addition, the hydroxide ions formed on the cathode will increase water pH and lead to the sedimentation of metal ions as the responsible hydroxides and simultaneous sedimentation with Fe or Al hydroxides.

$$Me^{n+} + nOH^{-} \rightarrow Me(OH)_{n(s)}. \qquad (5)$$

c) *The coagulation of unstable phases as clots.* In the next step, anode metal ions and hydroxide ions formed on the surface of the electrodes in water, reacted with different forms of hydroxide, and produced polymers.

$$Al^{3+} + 3OH^{-} \rightarrow Al(OH)_{3(s)}, \qquad (6)$$

$$nAl(OH)_{3(s)} \rightarrow Al_n(OH,)_{3n(s)}$$

$$2Fe^{2+}_{(aq)} + 3/2O_2 + 3H_2O \rightarrow 2Fe(OH)_{3(s)},$$

$$nFe(OH)_3 \rightarrow Fen(OH)_{3n}.$$

The pros of the EC process include its high efficacy in removing organic and non-organic pollutants (Biochemical Oxygen Demand (BOD), oils, dyes, heavy metals, and minerals), its condensed treatment facilities, relatively low cost, and complete automatic control [10]. This study aims to find an appropriate and effective way to remove hardness from drinking water by evaluating the efficacy of the EC process with direct and alternating currents and using Fe and Al rod electrodes in removing water hardness and studying factors effective in the process.

2. Materials and methods

2.1. The water sample and its characteristics

The water sample in this study was supplied by the water distribution network of Damdaran at the city of Zahedan. There is no proper drinking water in this area. The collected samples were kept at 4°C while being transferred to the laboratory. The characteristics of the water used in this study are seen in Table 1.

2.2. The material and equipment used

The chemicals used in this study include ammonium buffer solution, Al buffer, eriochrome black-T, Murexide, Ethylene Diamine Tetra Acetic (EDTA) acid, chloridric acid (HCl), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), phenolphthalein indicator, methyl orange indicator, Ortho-phenanthroline, ammonium acetate buffer, and Hydroxylamine, all of which are characterized by the Merck brand. The equipment cases used in this study include an accurate electrical scale (FG-H model), a desiccator (Simax model), a turbidity meter (model TU-2016), a spectrophotometer (model AL800), a conductivity meter (model 4071), a pH meter (InoLabWTW model), a crucible (Mindex model), and a filter paper.

2.3. The construct of the EC cell

In this study, the EC experiments were performed in the batch mode using a reactor made of plexiglass sheets with 110 × 130 × 140 mm dimensions. The efficient volume of the reactor was 1.5 L. The electrodes used were made of Fe and Al with different arrangements of Fe-Al and Al-Fe, the purity of Fe and Al was 98.5%, and 40 rods were built with a diameter of 1 cm and a height of 15 cm. The effective surface of the electrodes was 31 cm^2. The distance between the electrodes is an effective parameter in the EC process in the 1–3 cm range under study. The electrodes connect to each other in a series based manner and, also, to a direct or alternating power supply within a monopolar range of 1–12 mA/cm^2 (connecting only two rows of side electrodes to positive and negative poles=MP-S). The polarity of the electrodes changed automatically by a polarity inverter every 120 seconds and for 30 seconds. Electrodes were 2 cm away from the base of the reactor. This was done for better mixing and preventing high potential mass transfer in the EC reactor. A schematic graph of this cell is shown in Figure 1(a) and (b).

Table 1. The characteristics of the drinking water sample used in this experiment.

	Parameter	Amount	Unit
1	Total hardness	690	mg/L $CaCO_3$
2	Ca hardness	315	mg/L $CaCO_3$
3	Mg hardness	375	mg/L $CaCO_3$
4	Phenolphthalein alkalinity	32	mg/L $CaCO_3$
5	Methyl Orange alkalinity	438	mg/L $CaCO_3$
6	Turbidity	4.72	NTU
7	Color	13.15	TCU
8	TDS	1643	mg/L
9	EC	2385	μs/cm
10	pH	8.74	–
11	Fe	3.71	mg/L
12	Al	2.54	mg/L

2.4. Experiments

The pH of the sample was set by sulfuric acid and 1 normal NaOH. After setting the pH to a range of 4–10 (e.g., 4, 5, 6, 7, 8, 9, and 10), samples were injected into the EC reactor. In addition, after connecting to electrical current at a density of 1–12 mA/cm^2 (e.g., 1, 3, 6, 9, and 12 mA/cm^2) using alternating and direct currents with different arrangements of Fe and Al rods at time intervals of 3–24 min (e.g., 3, 6, 12, and 24 min) at the stirring speeds of 200-500 rpm (e.g., 200, 300, 400, and 500 rpm) at room temperature, sampling was done from the middle of the reactor. The samples taken were filtered through a membrane filter with 0.45-micrometer pores to remove

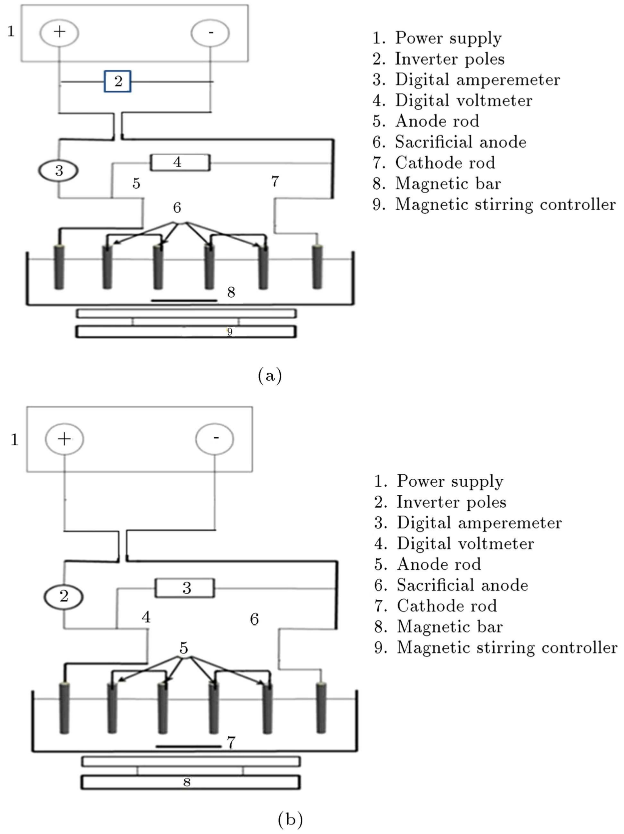


Figure 1. Schematic diagram of the electrocoagulation reactor: (a) With polarity inverter, and (b) without polarity inverter.

the formed clots. The filtered samples were analyzed for total hardness and calcium hardness. The pH of the solution inside the reactor was analyzed at the end of the experiment. After every exam, the electrodes were washed with thin HCl solution and, then, washed with distilled water and weighted accurately. The weight of electrodes before and after the process was determined in order to estimate the amount of the sacrificial electrodes. Moreover, the amount of used energy and sludge produced was also calculated.

2.5. Analysis and calculations

All water quality analyses were carried out according to the standard methods book [11]. The hardness of the water sample was determined by the EDTA Titrimetric method, the alkalinity by potentiometric titration, turbidity by nephelometry, color by photometry, electrical conduct with a conductivity meter, Total Dissolved Solid (TDS) by gravimetry, pH by a pH meter, and Fe and Al by photometry. In addition, energy consumption (which is an important economic parameter in the EC process) and electrode consumption were calculated.

3. Results and discussion

3.1. The effect of electrode type, their arrangement, and polarity inverter

The electrode of the electrochemical cell is the core of the reactor. Therefore, choosing the right material and right electrode pair is very important and is known as an effective factor in the process performance. The most common materials for electrodes in electrocoagulation are Fe and Al. They are cheap, accessible, and of course effective. In this study, in order to determine the optimum electrode pair, Fe and Al rods in two different arrangements of Fe-Al and Al-Fe were evaluated for removing the hardness of drinking water at 25°C and in similar conditions. Figure 2(a), (b), Figure 3(a), (b), and Table 2 show the effect of different pairs of electrodes with and without the polarity inverter (current density of 6 mA/cm^2, stirring speed of 200 rpm, distance of 1 cm between electrodes) on the efficacy of removing total hardness and Ca hardness. According to these figures, a relatively high efficiency rate was achieved with Fe-Al pair electrodes (Fe as anode and Al as cathode) with the polarity inverter. The efficiency rate of hardness removal with paired Fe-Al electrodes using alternating current and in the electrolysis time duration of 24 min was 95.95% for total hardness and 85.26% for calcium hardness. In addition, through direct current, the aforementioned rate was computed at 94.34% and 83.02% for total and calcium hardness, respectively. Further to this, the efficiency with paired Al-Fe electrodes using alternating current and with the polarity inverter for total hardness and calcium hardness was 91.04% and 80.18%, respectively. Through direct current, the efficiency with the polarity inverter for total and calcium hardness was 90.16% and 78.05%, respectively. The high efficiency for the Fe-Al paired electrode seems to be related to the chemical reaction, which occurs at the anode [12].

For the Fe anode:

$$Fe \rightarrow Fe^{2+} + 2e^{-}. \tag{7}$$

For the paired Al-Fe electrode, the chemical reaction that occurs in the anode is:

For the Al anode:

$$Al \rightarrow Al^{3+} + 3e^{-}. \tag{8}$$

In the initial stage, Fe and Al ions are very efficient coagulants for coagulating particles. From the two reactions above, the equivalent electrochemical mass for

Table 2. The efficiency of removing total and calcium hardness by the electrocoagulation process in different electrode arrangements using alternating and direct currents without polarity inverter.

Electrode and current type	EC time (min)	pH						Electrode and current type	EC time (min)	pH					
		5		7		9				5		7		9	
		TH	CH	TH	CH	TH	CH			TH	CH	TH	CH	TH	CH
Fe-Al, alternative current	3	9.53	6.72	23.35	14.56	38.29	32.16	Fe-Al, direct current	3	6.92	4.89	14.32	10.73	31.25	24.15
	6	20.18	16.11	48.17	35.13	71.93	53.18		6	18.71	13.24	39.15	24.18	49.12	39.81
	12	38.44	30.71	71.42	51.77	82.15	69.25		12	33.12	27.53	63.19	40.19	78.69	58.69
	24	45.85	38.19	79.84	63.21	86.37	76.31		24	40.16	34.18	71.59	56.64	83.72	71.26
Al-Fe, alternative current	3	12.53	8.76	24.13	17.74	22.79	14.93	Al-Fe, direct current	3	12.32	8.93	18.25	13.42	17.44	11.24
	6	28.16	15.19	47.59	33.18	40.16	30.13		6	25.51	17.57	46.73	32.27	36.16	26.17
	12	57.34	38.45	66.32	51.34	53.81	42.26		12	55.76	36.18	69.15	53.86	51.38	42.82
	24	68.72	51.88	83.11	68.26	64.12	56.61		24	62.14	48.35	78.95	67.22	59.14	54.19

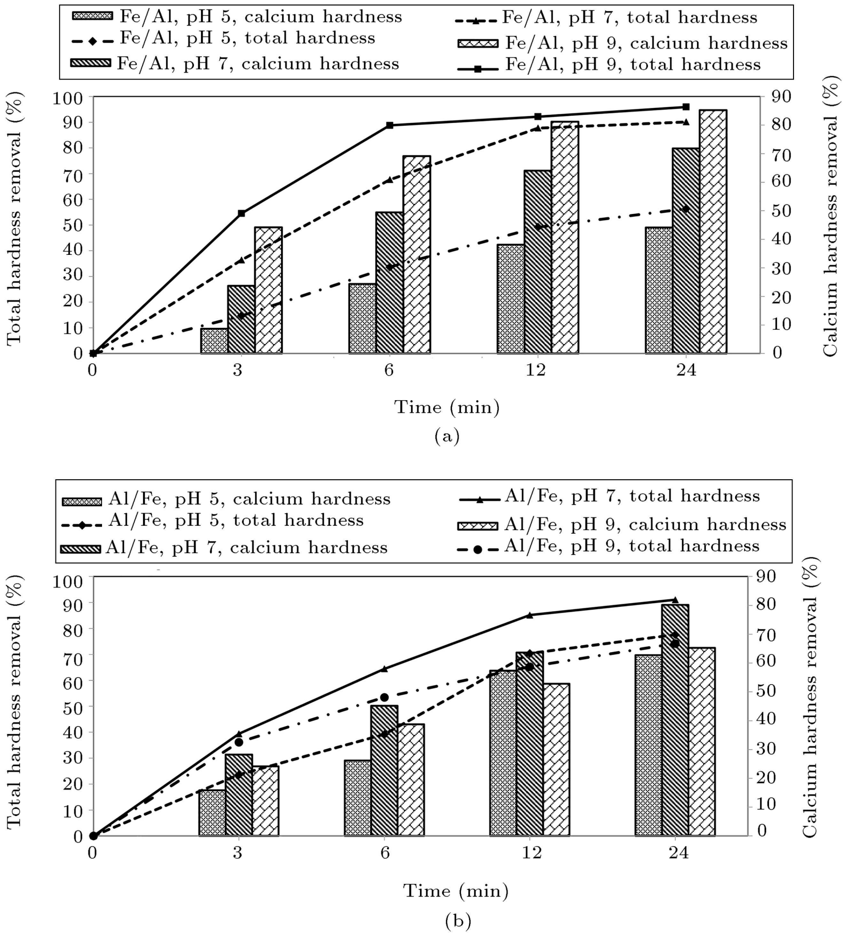


Figure 2. The efficiency of removing total and calcium hardness by the electrocoagulation process in different electrode arrangements using alternating current and polarity inverter: (a) Fe-Al electrode arrangement and (b) Al-Fe electrode arrangement.

Fe and Al can be estimated. Therefore, the equivalent electrochemical mass for Al was 335.6 mg/Ah and for Fe was 1041 mg/Ah, which is three times the mass for Al. Consequently, when an equal electrical charge passes, more coagulants are theoretically produced from the Fe anodes than from the Al anodes. This is probably the reason for the higher removal efficiency for Fe electrodes [13]. According to Figure 2(a), (b) and Figure 3(a), (b), the percentage of total hardness and calcium hardness removal is affected by the arrangement of the electrodes. An Fe anode with different types of cathode was found to be more able than an Al anode to reduce the total and calcium hardness of water. Therefore, the type of cathode plays an important role in removing total and calcium hardness of water; in this study, the Al cathode showed better efficacy. The results showed that an assured electrode arrangement may be practically more efficient or economical for certain purposes. The better performance of Fe than Al as a sacrificial electrode is associated with the higher oxidation potential of Fe (−0.447 V) than that of Al (−1.662 V); therefore, the oxidation rate for Fe is higher than that for Al [14]. The higher efficacy of the Fe-Al arrangement may be associated with the high gradient of the electrode potential and, thus, the higher oxidation potential between the anode and cathode than other arrangements. This leads to the production of more coagulants and improvements to the percentage of pollutant removal [15]. The advantage of Fe in comparison to Al as a sacrificial electrode in the EC process has also been reported by other researchers in removing different pollutants. In their study on the removal of Indium ion through the EC process, Chou and Huang showed that Fe anode and Al cathodes represent an optimum electrode pair after 90-min electrolysis [16]. Further, on the removal of pollutants from tannery wastewater by the EC process, Benhadji et al. concluded that Al showed better performance as cathode than iron and steel [17]. In contrast, in a study on treating the paper mill wastewater with the EC process, Katal and Pahlavanzadeh [18] proved that Al electrodes showed better performance than Fe as a sacrificial electrode in the EC process. Therefore, the better arrangement and

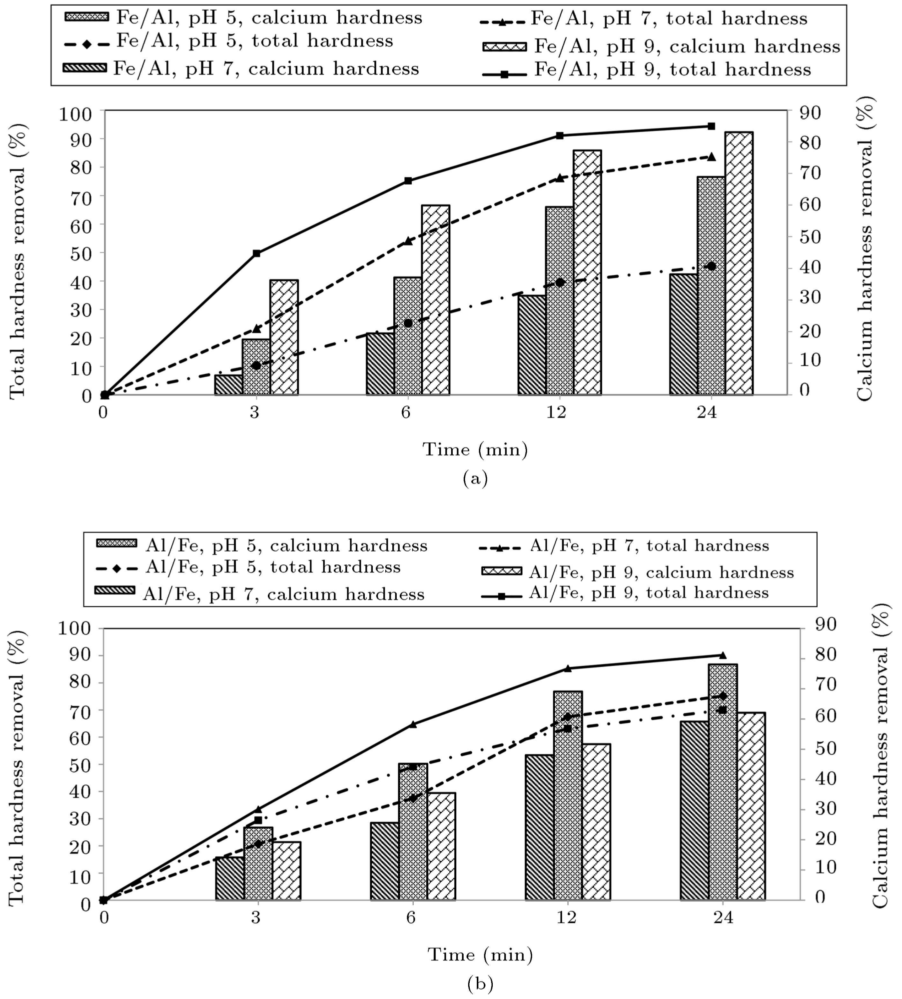


Figure 3. The efficiency of removing total and calcium hardness by the electrocoagulation (EC) process in different electrode arrangements using direct current and polarity inverter: (a) Fe-Al electrode arrangement and (b) Al-Fe electrode arrangement.

material used in the anode are very much related to the type of pollutant and its operating circumstances.

In studies that have considered the Fe electrode as anode, two mechanisms have been applied to produce metal hydroxides [18]:

Mechanism 1:

Anode:

$$4Fe \rightarrow 4Fe^{2+} + 8e^{-}, \tag{9}$$

Chemical:

$$4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8H^{+}. \tag{10}$$

Mechanism 2:
Anode:

$$Fe \rightarrow Fe^{2+} + 2e^{-}, \tag{11}$$

Chemical:

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2, \tag{12}$$

Cathode:

$$2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_2, \tag{13}$$

In total:

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2. \tag{14}$$

In oxygenated water and at low pH, Fe^{2+} is easily converted to Fe^{3+}. The $Fe(OH)_{n(S)}$ formed in aqueous environments remains as suspended jelly, which can remove waste material by making complexes or by electrostatic absorption after coagulation. The ferric ions produced electrochemically can be monomeric ions, hydroxy ferric complexes with hydroxide ions, and polymeric types, which are usually in the form of $Fe(OH)_2^{+}$, $Fe_2(H_2O)_6^{3+}$, $Fe(H_2O)_5OH^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe_2(H_2O)_8(OH)_2^{4+}$, $Fe(H_2O)_6(OH)_4^{2+}$, and

$Fe(OH)_4^-$; this depends on the range of pH. Therefore, the main mechanism for removing hardness salts from water by the EC process may include Fe oxidation to ferrous ions and water electrolysis on the surface of the anode that leads to oxygen production, the oxidation of the ferrous ions to ferric through reaction with oxygen molecules, and the formation of hydroxide, poly hydroxide, and insoluble polyhydroxy Fe oxide [19]. In treating the solution with Fe electrodes, the environment which was green at the beginning of the process turns yellow. At the end, while the flocks were forming, the filtered sample was clear. The green and yellow colors were derived from Fe^{2+} and Fe^{3+}, respectively. This color variation occurs because, during the electrolysis of Fe, the majority of ions produced were associated with Fe^{2+} which can be easily oxidated to Fe^{3+} in the presence of oxygen in water.

Concerning the Al electrode, as the anode, the OH^- ions were produced from water electrolysis on the surface of the cathode, while Al^{3+} ions were produced from the electrical analysis of the anode. They react with each other based on the reactions mentioned above and, thus, form $Al(OH)_3$ [20]:

Anode:

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-, \tag{15}$$

Cathode:

$$3H_2O + 3e^- \rightarrow 3/2H_2 + 3OH^-, \tag{16}$$

In total:

$$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_{3(s)}. \tag{17}$$

From the electrical analysis of Al as the anode at low pH, monomeric cation types including Al^{3+} and $Al(OH)_2^+$ are produced which convert to $Al(OH)_3$ at a suitable pH and, eventually, to $Al_n(OH)_{3n}$ polymers [21]:

$$nAl(OH)_3 \rightarrow Al_n(OH)_{3n}. \tag{18}$$

In the Al electrode during electrocoagulation, the monomeric types of $Al(OH)^{2+}$, $Al(OH)_2^{2+}$, $Al_2(OH)_2^{4+}$, $Al_2(OH)_2^{4+}$, $Al(OH)^{4-}$ and polymeric types of $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, and $Al_{13}(OH)_{34}^{5+}$ are formed, and the rate of the formation of these different types depends on the pH of the environment.

The electrochemical reactions at the cathode and anode include the reaction of hydrogen and oxygen changing forms, respectively. At a high pH, the hydroxides produced at the cathode react with the Al^{3+} produced at the anode and make different monomeric types. When Fe is used as the cathode, it cannot produce anionic hydroxide Fe when the pH is below 5 and the cathode will not corrode. However, when Al is used as the cathode and, also, because of its aqua-phobic characteristics, a significant increase in the pH close to the cathode occurs due to hydrogen production, which leads to a chemical attack on Al and its corrosion [18]:

$$2Al + 6H_2O + 2OH^- \rightarrow Al\,(OH)_4^- + 3H_2, \tag{19}$$

$$2Al + 3H_2O \rightarrow 2Al^{3+} + 3/2H_2 + 3OH^-. \tag{20}$$

$Al(OH)^-$ can react with cations and remove some pollutants by neutralizing their electrical charge or solubility, or it can change into irregular forms of $Al(OH)_3$ which coagulate with colloidal pollutants and be deposited as sediment.

$$[Al(OH)_4]^- \rightarrow Al(OH)_3 + OH^-. \tag{21}$$

When Al electrodes are used in the electrochemical and chemical processes, hydrogen is produced. The formation of metal hydroxides continues until the impurities of water are coagulated and hydrogen bubbles produce foam at the cathode, transferring pollutants to the solution surface and, then, separating them through floating. The effect of hydrogen produced at the cathode facilitates the accumulation of flocks on the surface of the solution in the shape of a thick whitish flower. At the end of the experiment, the filtered sample was clear and stable. The efficiency of removing pollutants extremely correlates to the size of the formed bubbles, which is related to the cathode and anode materials. Different types of chemicals are produced in the EC and the electro-flotation process by removing pollutants [22]. According to the results of investigating the type of electrode, its arrangement, and polarity inverter, the Fe-Al electrode pair with polarity inverter was chosen as a suitable arrangement to carry on performing the experiments.

Moreover, the electrochemical experiments were carried out without using polar inverters to evaluate their efficiency in the treatment process. As can be seen in Figures 2, 3 and Table 2, compared to the reactor without polar inverters arrangement, the EC reactor with polar inverters increases the removal efficiency of total hardness and calcium hardness by about 10% and 9% in the Fe-Al arrangement and by 8% and 12% in the Al-Fe arrangement using alternating current, respectively. In addition, the removal efficiency of total hardness and calcium hardness in the Fe-Al arrangement using direct current increases by almost 11% and 12% and by 11% and 10% in the Al-Fe arrangement, respectively.

One of the most important topics concerning the operation of the EC process is electrode deactivation.

The inactive layers of the electrode cause increased potential and energy waste in the EC process. The formation of one layer of oxide on the surface of the anode electrode prevents metal decomposition and electron transfer and limits the coagulant increase in the solution. Moreover, at high pH, there is a possibility of forming a layer of calcium carbonate and magnesium hydroxide on the cathode electrode. The thickness of these layers increases over time, while the efficiency of the EC process decreases [8]. When the poles are inverted, the position of the anode and cathode is switched; then, mineral deposition on them decreases and the durability of the electrodes doubles. The application of a polarity inverter can attenuate the oxide layer on the electrodes according to the following equations [23]:

$$Al_2O_3 + 6H^+ + 4e^- \rightarrow 2Al + 3H_2O, \tag{22}$$

$$Fe_2O_3 + 6H^+2e^- \rightarrow 2Fe + 3H_2O. \tag{23}$$

3.2. *The effect of initial pH*

The initial pH of the electrolyte is one of the important factors in the performance of the electrochemical process, especially the performance of the EC process, and has an important role in the efficiency of removing different pollutants. To evaluate its effect, a series of experiments were performed by setting the initial pH to a range of 4–10 by sulfuric acid and NaOH 1 normal and using the alternating current at a density of 6 mA/cm^2 and the Fe-Al electrode arrangement during 3–24 min for decreasing salts, which cause hardness in drinking water. Table 3 shows the effect of water pH on the removal of total and calcium hardness through the EC process (using alternating current, Fe-Al electrode arrangement, a current density of 6 mA/cm^2, stirring speed of 200 rpm, and 1-cm distance between electrodes). As can be seen, by increasing pH from 4 to 10, the removal efficiency of total hardness increased from 43.15% to 96.79% and from 30.25% to 87.13% for calcium hardness after 24 min operation time. Besides, the results in Table 3 show that many changes were not seen in the 8–10 pH range while removing both types of hardness, and the remaining EC experiments were performed at pH=9, which is close to the pH of drinking water. Therefore, the pH of the sample entering the EC cell required minor toning.

As mentioned above in the EC process, pH does not have a significant effect on the formation of metal hydroxide types and the mechanism for removing ions and pollutants. In three pH ranges of acidic, neutral, and alkaline which were evaluated in this study, reactions are given below [6]:

At acidic pH:

$$2Fe_{(s)} + 6H_2O_{(l)} \rightarrow O_{2(g)} + 4H_{2(g)} + 2Fe(OH)_{2(s)}. \tag{24}$$

At neutral pH:

$$3Fe_{(s)} + 8H_2O_{(l)} \rightarrow Fe(OH)_{2(s)} + 2Fe(OH)_{3(s)} + 4H_{2(g)}, \tag{25}$$

At alkaline pH:

$$2Fe_{(s)} + 6H_2O_{(l)} \rightarrow 2Fe(OH)_{3(s)} + 3H_{2(g)}. \tag{26}$$

In addition to the above reactions, other reactions might also occur in high acidic conditions at the cathode, which are as follows:

$$HCO_3 + OH^- \rightarrow CO_3^{2-} + H_2O, \tag{27}$$

$$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3, \tag{28}$$

Table 3. The effect of initial pH on the efficiency of total and calcium hardness removal and its changes during the electrocoagulation (EC) process.

Efficiency of removal	**Electrode and current type**	**EC time (min)**	**Initial pH**						
			4	5	6	7	8	9	10
Total hardness removal	Fe-Al, alternative current	3	9.41	14.72	21.18	36.41	47.75	54.52	56.8
		6	17.14	33.63	34.06	67.63	70.16	88.77	80.73
		12	29.36	49.18	46.24	87.7	90.73	92.15	94.4
		24	43.15	50.34	64.18	90.21	95.17	95.94	96.79
Calcium hardness removal	Fe-Al, alternative current	3	6.19	8.7	14.63	23.71	35.8	44.18	49.4
		6	11.62	24.35	25.32	49.44	59.87	69.11	68.15
		12	21.13	38.14	38.13	64.07	76.32	81.19	81.6
		24	30.25	44.11	53.14	71.82	83.21	85.27	87.13
Final pH			7.8	8.6	9.2	9.7	10.2	10.4	10.46

$$CO_3^{2-} + Mg^{2+} \rightarrow MgCO_3. \tag{29}$$

In these reactions, the produced H_2 moves upwards and causes floating and sedimentation of $Fe(OH)_2$ and $Fe(OH)_3$. Table 3 shows the pH of electrolytes after electrolysis compared to the initial pH. As can be seen, the pH of drinking water has changed during the EC process and increased. When the initial pH is ≤ 8, the increase in pH is greater; however, when the initial pH is > 8, the increase becomes trivial. This increase in pH is associated with the production of H2 gas at the cathode electrode and the accumulation of the hydroxide ions in the solution [24]. Further, this increase in pH is associated with the release of CO_2 from water or wastewater to hydrogen bubbles disturbance. At low pH, CO_2 in water is hyper saturated and can be released when hydrogen is being transformed, leading to an increase in pH. These results are in accordance with the previously published work, showing that EC demonstrates buffering capacity because it creates an equilibrium between OH-production and consumption which prevents significant changes in pH [6,24].

3.3. The effect of current density and type of current on the process efficiency and electrolysis voltage

In all electrochemical processes, the current density is the most important parameter for controlling the reaction rate inside the electrochemical reactor. It has been clearly seen that the amount of metal coagulant added to water (the amount of Fe and Al ions released by the anode) and controlling bubble production, its amount, and distribution is directly related to current density used for the process which, therefore, affects the growth of flocks in the EC reactor with different arrangements of electrodes [25]. The effect of current density on removing total and calcium hardness from drinking water was evaluated by two types of direct and alternating current with Al-Fe electrode arrangement. Fe-Al electrode arrangement with an area of 50 cm^2 was evaluated using direct and alternating currents separately with a current density within the 1-12 mA/cm^2 range for 24 min. The percentage of total and calcium hardness removal for different currencies is shown in Table 4 (conditions: pH = 9, stirring speed = 200 rpm, and distance between electrodes = 1cm). The results showed that alternating current with Fe-Al arrangement removed hardness more than direct current, and this is probably related to the monotonous analysis of the anode and cathode in alternating current during EC.

Moreover, the results show that with an increase in current density, total and calcium hardness decreases to a greater degree, because as current density increases, the amount of Fe and Al degradation at the anode increases and the density of metal ions in the solution increases; therefore, the hardness removal rate increases, too. Further, an increase in current density leads to more and smaller bubble production which causes greater upward current and faster removal of hardness salts by floating with hydrogen [26].

According to Faraday's Law in Eq. (30), the current density is directly related to the amount of absorbent formed electrochemically (Al or Fe hydroxides). Eq. (30) is given below [24]:

$$C_{elec,theo} = \frac{It_{EC}M_w}{zFv}, \tag{30}$$

where $C_{elec,theo}$ (kg of Fe or Al electrode/m^3 of treated drinking water) is the theoretical amount of ions produced by the passing current I (A) at a specific operation time t_{EC} (s), Z is the number of electrons involved in the oxidation/reduction reaction (for Fe = 2 and for Al = 3), M_W is the molecular weight of the anode material ($M_{W,Fe}$ =0.055 85 kg/mol, $M_{W,Al}$ =

Table 4. The effect of current density and type of current on the efficiency of removing total and calcium hardness with the electrocoagulation (EC) process.

Efficiency of removal	**Electrode and current type**	**EC time (min)**	**Current density (mA/cm^2)**					**Electrode and current type**	**EC time (min)**	**Current density (mA/cm^2)**				
			1	3	6	9	12			1	3	6	9	12
Total hardness removal	Fe-Al, alternative current	3	18.35	33.21	54.52	61.37	64.15	Fe-Al, direct current	3	13.83	24.46	49.63	56.73	59.34
		6	32.19	44.53	88.77	80.41	85.82		6	24.51	39.52	75.15	77.51	81.58
		12	50.62	68.27	92.15	98.26	96.18		12	46.17	61.25	91.05	93.48	94.07
		24	56.48	74.38	95.94	98.93	97.33		24	51.38	69.14	94.34	95.16	95.64
Calcium hardness removal	Al-Fe, alternative current	3	10.51	21.17	44.18	49.73	53.28	Al-Fe, direct current	3	7.63	13.52	36.28	44.29	47.51
		6	19.39	35.54	69.11	71.18	74.46		6	16.72	28.47	59.87	64.64	60.73
		12	37.64	55.16	81.19	87.69	85.30		12	30.91	49.31	77.29	80.23	84.06
		24	42.58	62.49	85.24	89.14	87.31		24	37.14	54.82	83.04	86.52	87.12

0.026 98 kg/mol), F is the Faraday constant (964 85 C/mol), and V is the volume (m^3) of drinking water in the EC reactor. Therefore, the adsorption amount of salts causing hardness increases with increased concentrations of the absorbent, and shows that adsorption is related to the accessibility of the bond in the Fe or Al hydroxide flocks for hardness salts [27]. According to the results of this study, the current density of 9 mA/cm^2 was chosen as the optimum.

An insignificant increase in removing total and calcium hardness with an increase in current density (more than 9 mA/cm^2) is more likely due to the adsorption of oxygen bubbles produced by the anode, which are set horizontally under the cathode. Although they will eventually be destroyed, they become adsorbed at a level lower than the cathode [6].

Low current density in not enough for optimal separation; however, the possibility of film production on the surface of the anode decreases. Higher current density causes better soluble pollutant removal. If the amount of soluble pollutant is high, the removal process gradually decreases due to the accumulation of a gelatinous Fe and Al hydroxide film on the anode, even by using high density current. Further to that, with an increase in current density, electrolysis time shortens. For example, when current density increases from 1 to 9 mA/cm^2, the time of water electrolysis in the electrocoagulation units reduces from 24 to 3 min. This means that the EC equipment at a current density of 9 mA/cm^2 can be 8 times smaller than that at a current density of 1 mA/cm^2. Of course, with an increase in the current density, electrolysis voltage and its power experience an increase. These results are consistent with the finding of Vasudevan et al. [28] on the removal of chromium from drinking water through the EC process and, also, with the study of Matias et al. [29] which investigated the removal of silver nanoparticles from wastewater through the EC process.

The relation between electrolysis voltage and current density is shown in Figure 4 (by using electrode arrangement Fe-Al, pH = 9, stirring speed = 200 rpm, distance between electrodes = 1 cm, and electrolysis time = 12 min). As can be seen, the electrolysis voltage and power increases linearly as current density increases. Increasing current density from 1 to 12 mA/cm^2 causes an increase in voltage between electrodes from 1.95 V to 11.47 V and an increase in the necessary power from 0.19 to 1.12 kWh/m^3 using alternating current and from 0.54 to 3.06 kWh/m^3 using direct current. Therefore, there is an optimal current density for decreasing the total costs of investment and operation, the accurate range of which depends on the geographical and economic circumstances of the place where EC is used. As can be seen above, for the drinking water of the area under study, in a situation where the necessary power is less than 3.5 kWh/m^3, the density of optimum current is 9 mA/cm^2. These results are similar to the study of Chou and Huang [16] that removed indium ions from aqueous solution by EC and, also, to the study of Mouedhen et al. [21] that evaluated the reaction of Al electrodes in the EC process.

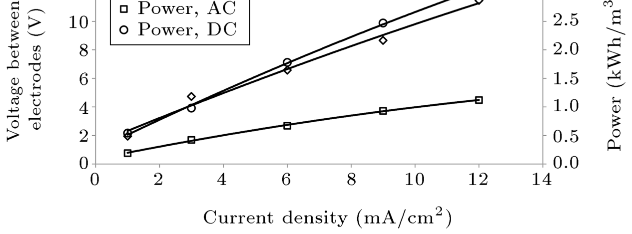


Figure 4. The changes in electrolysis voltage and power as the result of density and current type.

3.4. The effect of electrolysis time

One of the important parameters effective in the EC process operation and the economic application of this process is the time of the EC process. According to Faraday's Law, the amount of Fe or Al released in the EC system using Fe or Al electrodes can be related to the electrolysis time, which can increase the Fe or Al ions released in the system [24]. During the EC process, the time provided is for producing metal hydroxides and completing the coagulation of impurifications [30,31]. The EC experiments were done during 24 min using alternating and direct currents at different current densities. Table 4 shows the relationship between time of reaction and the efficiency of removing total and calcium hardness. As can be seen in the table, by using both types of current and increasing the electrolysis time, the efficiency of total and calcium hardness removal increases. By using alternating current, at a current density of 9 mA/cm^2, the efficiency of total and calcium hardness removal increased from 61.37% to 98.26% and from 49.73% to 87.69%, respectively, during 3 to 12 min. Through direct current with the same current density and electrolysis time, the efficiency of removing total hardness and calcium hardness changed from 56.73% to 93.48% and from 44.29% to 80.23%, respectively.

This phenomenon is related to this fact that the electrolysis time determines the production rate of Fe^{3+} and Al^{3+} from the Fe and Al electrodes. The efficiency of pollutant removal is directly related to the density of hydroxide and metal ions produced at the electrodes. During the time of electrolysis, the positive electrode faces anode reactions. The released ions neutralize the electrical charge of the pollutants and, therefore, coagulation starts. When the time of electrolysis increases, the density of ions and hydroxide clots increases as well; hence, the removal efficacy increases [32]. These results are in line with those of Kuokkanen et al. [33] on the treatment of runoff from the coal swamp containing humic acid using EC and with those of Murthy and Parmar [34] about the removal of strontium by the EC process.

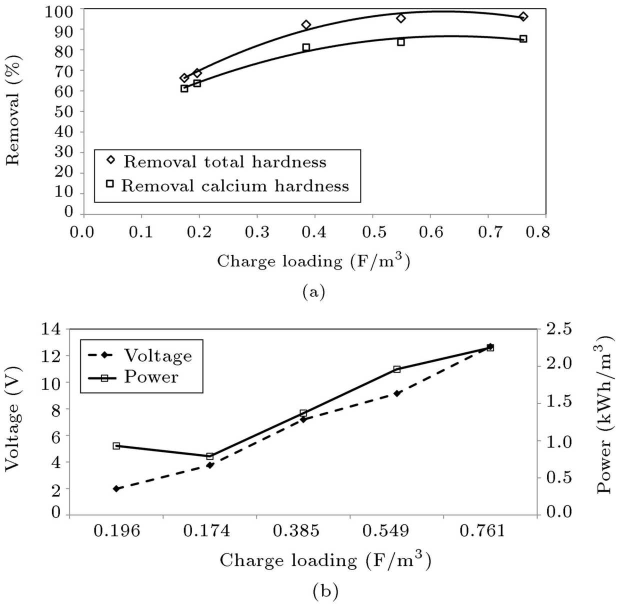
The removal efficiency for both types of hardness using alternating or direct currents after 12 min of electrolysis did not change much. This fact may relate to the surface of cathode reduction and the formation of new electrocoagulation flocs [25]. Therefore, in the present study, the electrolysis time of 12 min was chosen as the optimum.

3.5. The effect of charge loading

The mechanisms of the EC process for treating water and wastewater are quite complicated. In general, there are three probable mechanisms besides electrocoagulation: electroflotation, electrochemical oxidation, and adsorption. However, almost all mechanisms are severely related to charge loading [8]. Charge loading is the electrical quantity per unit of volume. In the EC process, Fe^{2+} or Al^{3+} coagulants are produced by electrochemically sacrificing Fe or Al electrodes. Their dosage is determined by charge loading. The quality of the EC process in treating wastewater is related to the amount of coagulant produced or the charge loading applied. Theoretically, according to Faraday's Law, whenever one Faraday electrical charge passes the circuit, 9 g of Al or 28 g of Fe from each anode in different connecting modes dissolves during the EC process. When the charge loading of the EC process is low, the dosage of coagulates (Al^{3+} or Fe^{2+}) for removing all ions causing hardness is enough. Therefore, the efficiency of removing hardness is not high. Charge loading (Q in F/m^3) is calculated by multiplying the current used in the EC process by the operation time according to Eq. (31) [35]:

$$Q = \frac{It_{EC}}{Fv}. \tag{31}$$

The amount of charge loading required for hardness removal (conditions: alternating current, Fe-Al electrode arrangement, a current density of 9 mA/cm^2, pH of 9, stirring speed of 200 rpm, 1-cm distance between electrodes, and electrolysis time of 12 min) is shown in Figure 5(a). Removing hardness is proportionate to charge loading in the range of 0.1–0.8 F/m^3. To analyze the relationship between charge loading and removal efficiency, it can be seen that removal efficiency initially increases rapidly with increasing charge loading; however, while charge loading increases, the removal efficiency rarely increases. In the monopolar series (MP-S) connection mode, in order to remove hardness, the removal curve above the amount of charge loading, which is approximately 0.54 F/m^3 (removal efficiency of total hardness and calcium hardness being 98.26% and 87.69%, respectively), turned flat. In this situation where the loading of the optimum charge must increase by the final stage, this amount of charge loading will be considered as the optimum amount. The main mechanism for removing ions producing hardness before charge loading reaches its optimum is electrocoagulation. Minimal improvement in removing ions causing hardness following an increase in charge loading is probably the result of adsorption and electrochemical oxidation, which is not worth the energy it uses because of the rapid increase in electrolysis voltage (Figure 5(b)) [36].



(a)

(b)

Figure 5. (a) The effect of charge loading on the efficiency of removing total hardness and calcium hardness, (b) The effect of charge loading on the electrolysis voltage and necessary power with electrocoagulation (EC).

Therefore, most of the Al^{3+} and Fe^{2+} ions added at a low density of ion causing hardness are used for removing the remaining hardness. The higher densities of Fe^{2+} on the surface at the anode can facilitate removing the ions that cause hardness by making complexes, adsorption, and sedimentation. Mass transfer for this density can be limited by increasing gas production using higher current. The other reason is that pressure on the lower parts of electrodes with a relatively high electrical circuit around them is conducive to the corrosion of those parts at a much faster rate than other parts of the electrodes, and this can lead to the waste of Al or Fe and electricity due to the loss of dissolved Fe or Al in the effluent, which results in a lower slope, as shown in Figure 5(a). These results are in line with the study results of Kobya et al. [8] about the removal of arsenic from drinking water by batch and continuous electrocoagulation processes and with those of Irdemez et al. [37] about the removal of phosphate from wastewater with the EC process. In total, hardness removal which is dependent on the applied charge loading shown in Figure 5(a) shows that the EC process has been applied at an acceptable level.

3.6. The amount of energy and electrode consumption

It is clear that a technically efficient process must be practically economical, too. The amount of energy consumption is an important economic parameter in the EC process, and the majority of operation costs of this process are related to electrical energy consumption. Although increasing current density and operation time increases the efficiency of EC, it also increases the voltage, the energy used, and the operation costs [24]. Consequently, evaluating the consumption of energy is necessary for treating water and is used to determine if EC is appropriate regarding its costs for removing the ions that cause hardness in drinking water. The electrical energy required for removing ions causing hardness in the Fe-Al connected mode in kWh/m^3 is calculated through Eq. (32) [38]:

$$E = \frac{U.I.t_{EC}}{V}, \tag{32}$$

where E is the energy consumption (kWh/m^3), U is the voltage used (V), I is the current (A), t_{EC} is the electrolysis time (s), and V is the volume of the sample (m^3). In Figure 6, considering Fe-Al electrode arrangement, pH of 9, electrolysis time of 12 min, stirring speed of 200 rpm, and 1-cm distance between electrodes, the density of the current (1–12 mA/cm^2) is depicted in comparison to the energy consumption. According to Table 4 and Figure 6, by using alternating current when current density increased from 1 to 12 mA/cm^2, during optimum electrolysis time of 12 min, the efficiency of total hardness and calcium hardness removal increased from 50.62% to 96.18% and from 37.64% to 85.30%, respectively, and energy consumption increased from 0.19 to 1.27 kWh/m^3 (Figure 6). When current density increased from 1 to 9 mA/cm^2, the efficiency of removing total hardness and calcium hard increased from 50.62% to 98.26% and from 37.64% to 87.69%, respectively; however, the energy consumption increased slightly (from 0.19 to 0.90 kWh/m^3). Nevertheless, when current density increased from 9 to 12 mA/cm^2, the efficiency of total hardness and calcium hardness removal increased slightly from 98.26% to 98.93% and from 87.69% to 89.14%, respectively, although the used energy increased from 0.9 to 1.27 kWh/m^3. Energy consumption was low using alternating current during the electrolysis process. Through direct current, when the current density increased from 9 to 12 mA/cm^2, the efficiency of total hardness and calcium hardness removal increased slightly from 93.48% to 94.07% and from 79.13% to 84.06%, respectively, although energy consumption increased significantly from 2.47 to 3.25 kWh/m^3. Therefore, the current density of 9 mA/cm^2 using alternating current provides optimal conditions for EC, and the result is reasonably efficient with low energy consumption.

Increase in current density due to polarization leads to increased energy consumption and increased total hardness and calcium hardness removal. Therefore, to reach optimum current, both the percentage of the removal and usage of energy should be evaluated. These results are in line with those of Ghosh et al. [39] about removing Fe from drinking water by EC and with those of Şengil et al. [14] about treating tannery wastewater [14,39].

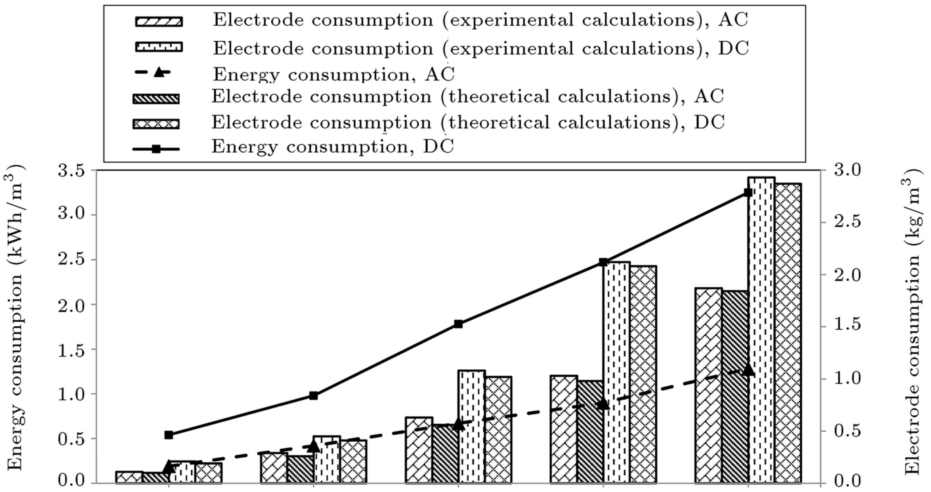


Figure 6. The amount of energy and electrode consumption in removing total and calcium hardness at different densities and currents during the electrocoagulation (EC) process of drinking water.

At high current density, the formation of Al and Fe complexes increases and, thus, the removal efficiency increases, too. This result notably reduces the weight of the electrode and increases electrical energy usage. Therefore, the dosage of Fe or Al released by the anode electrode is related to the duration of electrolysis and the current density. Therefore, current density and operation time in the EC process are among the most important parameters effective in the removal efficiency and controlling the reaction rate in the EC reactor [40]. The amount of electrode consumption (kg of Fe or Al per m^3 of treated drinking water) can be calculated theoretically using Faraday's Law (Eq. (32)) and is shown in Figure 6.

After each experiment, electrodes were cleaned, dried, and weighted and the amount of electrode dissolved at different densities was evaluated. A significant amount of weight loss observed was solely because of anode analysis. The amount of electrode used in the experiments at different current densities and optimum electrolysis times (12 min) is shown in Figure 6. At an optimum density of 9 mA/cm^2, through alternating current, the amount of electrode used was theoretically equal to 0.98 kg/m^3 and experimentally equal to 1.03 kg/m^3. Through direct current, the amount of electrode used was theoretically 2.08 kg/m^3 and experimentally equal to 2.12 kg/m^3. Through Eqs. (30) and (32), it can be estimated that energy and electrode consumption increases as current density and electrolysis time increase. These results are similar to those of Kobya et al. [8] about treating drinking water containing Arsenic with EC and to those of Ozyonar and Karagozoglu [41] about the treatment of pretreated coke wastewater by electrocoagulation and electrochemical peroxidation processes.

3.7. The effect of the distance between electrodes

The effect of the distance between electrodes on improving the removal of salts was evaluated. The distance between electrodes in a batch system is defined as the time of treatment for reaching a desirable rate of EC efficiency. When the distance between electrodes increases, electrical current decreases; besides, to reach a secure current density, the voltage must increase [6]. In the present study, through direct and alternating currents, the effect of the distance between electrodes (anode and cathode rods) equal to 1, 1.5, 2, 2.5, and 3 cm was evaluated. According to Table 5, in optimum conditions (Fe-Al electrode arrangement, a current density of 9 mA/cm^2, charge loading of 0.54 F/m^3, pH of 9, electrolysis time of 12 min, stirring speed of 200 rpm, and 1-cm distance between electrodes) using both alternating and direct currents, the best efficiency was achieved at a 1-cm distance; further to this, by increasing the distance between electrodes, the removal efficiency decreased. This high efficiency at a close distance of electrodes is probably achieved due to the electrostatic effects related to the distance between electrodes. Therefore, when this distance increases, the electrostatic effect decreases, the movement of the produced ions slows down, and there will be more time for coagulation and clot formation [24]. In other words, as the distance between the electrodes increases, the electrical resistance between electrodes increases and, therefore, ohmic drop or IR (Internal Resistance) drop increases, the accumulation of flocks weakens, and equivalently the adsorption of the pollutants decreases. Therefore, removal efficiency decreases. At the minimum distance between electrodes, resistance is lower which facilitates the electrolysis process and improves total and calcium hardness removal. Changes in the ohmic drop rate can be controlled through Eq. (33):

$$\eta \mathrm{IR} = \frac{I.d}{A.K}, \tag{33}$$

where I is current (A), d is the distance between electrodes (m), A is the active surface of anode m^2, and k is specific conduction (1000 ms/m^1). This equation shows that on a certain anode surface and electrical conduction, as the distance between the electrodes increases, the decrease in voltage accelerates, as well. For

Table 5. The effect of distance between electrodes on the efficiency of removing total and calcium hardness using different currents during electrocoagulation (EC) of drinking water.

Efficiency of removal (%)	**Electrode and current type**	**Electrode spacing (cm)**					**Electrode and current type**	**Electrode spacing (cm)**				
		1	1.5	2	2.5	3		1	1.5	2	2.5	3
Total hardness removal	Fe-Al, alternative current	95.26	92.37	91.43	87.51	85.48	Fe-Al, direct current	93.48	90.52	87.67	83.33	81.74
Calcium hardness removal	Fe-Al, alternative current	83.69	79.91	75.53	74.66	70.28	Fe-Al, direct current	80.13	78.19	73.59	70.25	65.36

the EC process, to use an acceptable amount of energy, increase in ohmic drop is not recommended. In order to ensure more than 90% removal of total hardness with the initial concentration of 690 mg/L and 80% removal of calcium hardness with the initial concentration of 315 mg/L, the optimum distance between electrodes was found to be 1 cm. In a study conducted by Naje et al. about treating textile wastewater with EC, the maximum removal efficacy for COD, TSS, and color was achieved when the distance between the electrodes was 1 cm [42]. Furthermore, in a study done by Mansoorian et al. about the removal of Pb and Zn from plating wastewater with EC, the maximum efficiency of removing heavy metals was achieved when the distance between the electrodes was 1 cm, too [24]. However, in a study done by Murthy and Parmar about the removal of strontium through the EC process, the removal efficiency increased as the distance between electrodes widened [34].

3.8. The effect of stirring rate

High stirring rates turn the ions toward the electrodes and lead to the formation of more products. Figure 7 shows the effect of stirring rate on the electrical sedimentation of total and calcium hardness through direct and alternating currents, Fe-Al electrode arrangement, optimum pH = 9, optimum current density = 9 mA/cm^2, charge loading = 0.54 F/m^3, electrolysis time = 12 min, and 1-cm distance between electrodes. As can be seen, the maximum efficiency of removing total and calcium hardness is achieved at 200 rpm, which is due to the formation and conjunction of flocks and, subsequently, their easier sedimentation, low stirring rates, and improved flotation. Decrease in the efficiency of the process at higher stirring rates results from the formation and appropriate separation of other salt sediments. Further, at a stirring rate of more than 200 rpm, external mass transfer becomes very trivial [15]. The mixing phenomenon, compared to a situation where flat electrodes stand beside each other, takes place better due to the production of more metal hydroxide clots at a certain time; the necessary time for performing the process shortens and the operation problems decrease, too. Therefore, to reach relatively sticky, but removable, sediment, 200 rpm is the optimum stirring speed. About the removal of phosphate using calcinated metal hydroxides, the sludge produced by EC, Golder et al. showed the highest removal efficiency at a stirring rate of 200 rpm [43]. However, concerning the removal of Cr salts from tannery wastewater, Sirajuddin et al. achieved maximum efficiency at a stirring rate of 500 rpm [44]. In addition, on the removal of nitrophenol from aqueous solution by EC, Modirshahla et al. found that as the stirring speed increased, the removal efficiency increased, too [45].

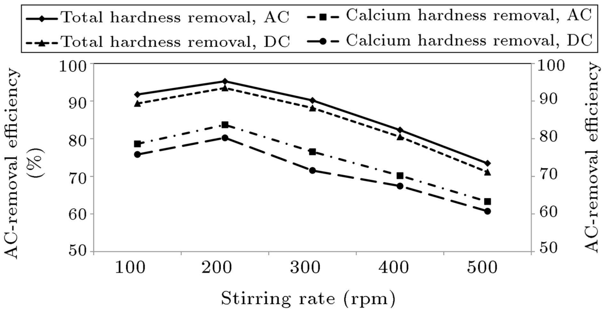


Figure 7. The effect of stirring speed on the efficiency of removing total and calcium hardness using different currents during electrocoagulation (EC) of drinking water.

3.9. The amount of sludge produced in the EC process and its settleability

Similar to chemical EC, most pollutants in water or wastewater do not disappear during electrocoagulation. Sludge is produced simultaneously with water or wastewater treatment. Sludge production is an important parameter for describing the EC process. In the EC process, about two thirds of the sludge floats on the surface of water or wastewater and runs out from one exit, although the rest of it is produced after sedimentation [46]. EC sludge production is linked to the characteristics of crude water or wastewater, sedimentable solids and material unstabilized by coagulation, coagulant concentration, current density, and electrolysis time. In addition to this, the sludge produced during EC is less toxic than the sludge produced by chemical EC because of the absence of additional chemicals [24]. The amount of sludge produced in the EC process for the monopolar parallel (MP-P) connection mode is shown in Figure 8 (using Fe-Al electrode arrangement, pH = 9, electrolysis time = 12 min, stirring speed = 200 rpm, and distance between electrodes = 1 cm). The amount of sludge produced using both alternating and direct currents increased with an increase in current density; however, this increase was found at a greater degree in the

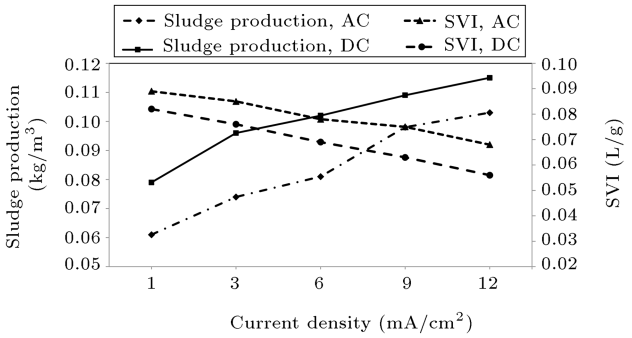


Figure 8. The amount of sludge produced and the Sludge Volume Index (SVI) in removing total and calcium hardness in different currents and current densities during electrocoagulation (EC) from drinking water.

case of direct current. Due to increase in the current density, the solubility of the anode becomes desirable, the remaining metal sludge increases, and the ions responsible for hardness are effectively removed from drinking water by both sedimentation and adsorption on metal sludge. The amount of sludge produced at a current density of 9 mA/cm^2 was 0.098 kg/m^3 using alternating current and 0.109 kg/m^3 using direct current. It appears that chemical or physical hydroxide Fe bonds with water are more than the hydroxide Al bonds. In a study done by Kobya et al. about treating arsenic-containing drinking water by EC, a minimum amount of sludge was produced in the monopolar series (MP-S) connection mode; in addition, it was 0.021 kg/m^3 for the Fe electrode and 0.017 kg/m^3 for Al [8].

The settleability of sludge may be explained through Sludge Volume Index (SVI), which is mainly used for the characterization of produced sludge. SVI is described as in Eq. (34) [9]:

$$SVI = \frac{H_{30}}{C_0.H_0} 1000 \left(\frac{ml}{g}\right), \tag{34}$$

where H_0 is the initial weight of the EC treated sludge in the settling column, H_{30} is the sludge weight after 30 min settling, and C_0 in g/L is the total concentration of sludge at $t = 0$ after EC treatment. By using Fe electrodes, the SVI using alternating and direct currents in the current density used is different. According to Figure 8, the amount of SVI was very low. By using alternating current, SVI at an optimum current density of 9 mA/cm^2 was 0.075 L/g; by using direct current at the same density, SVI was 0.063 L/g. The sludge produced by the Fe electrodes was heavy enough to produce a compact layer. When the current density increased, the size of sludge flocks increased; following the sedimentation, the layer of sludge became thinner and more compact. In a study done by Zodi et al. about the removal of non-biodegradable organic compounds and arsenic through Al electrodes, the amount of SVI at a current density of 100 A/m^2 was equal to 0.207 L/g and was 0.310 L/g at a current density of 150 A/m^2. However, with Fe electrodes, the amount of SVI at a current density of 100 A/m^2 was equal to 0.091 L/g and equal to 0.081 L/g at a current density of 150 A/m^2 [15].

4. Conclusions

Drinking water containing high hardness was softened by the EC process without the addition of chemicals. The effect of different parameters on the EC process and the efficiency of total and calcium hardness removal was evaluated. The results showed that the optimum removal efficiency rates of 98.26% and 87.69% were achieved for total hardness and calcium hardness using alternating current, respectively. Similarly, the optimum removal efficiency rates of 93.48% and 80.23% for total hardness and calcium hardness using direct current were achieved, respectively, in a condition characterized by an optimal current density of 9 mA/cm^2, pH = 9, electrolysis time of 12 min, optimal charge loading of 0.54 F/m^3, optimal stirring speed of 200 rpm, and optimal distance of 1 cm between electrodes using Fe electrodes as the anode and Al electrodes as cathode with the polarity inverter in the MP-S mode. Furthermore, the efficiency of this technology was evaluated by determining the amount of energy and electrode consumption, sludge produced, and Sludge Volume Index (SVI). The maximum amounts of energy and electrode consumption at the optimum current density were 0.9 kWh/m^3 and 1.03 kg/m^3 using alternating current and 2.47 kWh/m^3 and 2.12 kg/m^3 using direct current, respectively. The amount of sludge produced and SVI in the optimum condition were 0.098 kg/m^3 and 0.075 L/g using alternating current and 0.109 kg/m^3 and 0.063 L/g using direct current, respectively. According to the results of this study, electrochemical technology is very effective in the hardness reduction in desalination processes from water, which can overcome the drawbacks of the conventional processes.

Acknowledgement

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Nomenclature

Calcium	Ca
Magnesium	Mg
Iron	Fe
Aluminum	Al
EC	Electrocoagulation
$C_{elec,theo}$	Theoretical concentration of metallic cations in the electrolytic cell (kg/m^3)
I	Current (A)
t_{EC}	Electrolysis time (s)
M_W	Molecular weight of aluminum or Fe (kg/mol)
z	Valence ($zFe = 2$ and $zAl = 3$)
F	Faraday constant (964 87 C/mol)
V	Volume of the solution (m^3)
Q	Charge loading (F/m^3)
E	Energy consumption (kWh/m^3)
U	Voltage (V)
ηIR	Internal resistance drop

d	Distance between electrodes (m)
A	Active surface of anode (m^2)
k	Conductivity (ms/m^1)
SVI	Sludge Volume Index (L/g)
H_0	Initial weight of the EC treated sludge
H_{30}	Sludge weight after 30 min settling
C_0	Total concentration of sludge (g/L)

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