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Hardness removal of wastewater of power plant cooling tower using electrocoagulation system

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ABSTRACT

In this research, reducing and eliminating the hardness of wastewater of a power plant cooling tower was studied using an electrocoagulation system. For this purpose, a package with 1 m^3 capacity was designed and the hardness removal was investigated in a batch. The effect of current intensity (5–15 A/m^2), time (5–30 min), gap between electrodes (0.5–3 cm), pH (5–9) and ratio of surface of electrodes to volume of sample (S/V 15–45 m^2/m^3) were optimized using the experimental design method. According to response surface tests, the optimum range was obtained to maximize the removal efficiency of total hardness, both temporary and permanent hardness. The optimum values of studied factors were current density of 10 A/m^2, process time of 18.5 min, pH of 7.5, electrodes gap of 2 cm and S/V of 30 m^2/m^3. It was observed that the efficiency increased with increasing current density, time, pH and S/V, by 60% while, increasing the gap between the electrodes showed the opposite effect. However, the treatment efficiency of more than 90% and the energy consumption of less than 5 kWh/m^3 were obtained in optimum range of variables of current density 9.8–11 A/m^2, time 16.2–20.8 min, pH 7–7.8, the gap between the electrodes, 2 cm and S/V 27–33 m^2/m^3. In the optimal range, the hardness decreased from 1,430 to 109 mg/L, which indicates a high efficiency of 92%. Other factors such as sulfate (86%), chloride (85%) and total dissolved solids (97.9%) are also removed from the effluent at the same time.

Keywords: Electrocoagulation; Experimental design; Purification package; Hardness removal; Cooling tower

1. Introduction

The processes of coagulation and flocculation have been extensively used in water and wastewater treatment industry by involving a range of inorganic, organic, and hybrid materials [1–4]. Despite the long history of chemical coagulation in the water and wastewater industry, due to limitations such as high operating costs and adverse environmental impacts, there are no significant advantages [5,6]. Therefore, in order to find other suitable alternatives to replace the chemical treatment process, several approaches have been taken into consideration in recent years [5–8]. It is worth mentioning that electrocoagulation (EC) is an effective and eco-friendly alternative which does not require any chemical additives with simple operation and low maintenance [9–11]. Electrocoagulation involves the production of coagulants in situ by electrolytic oxidation of either aluminum (Al) or iron (Fe) ions from aluminum or iron electrodes called the sacrificial anode and hydrogen bubbles are generated around the cathode [5].

The presence of impurities in the water causes sediment in heating devices and boilers, which reduces the useful life of the device. As water is continually recirculated, the solubility of minerals such as calcium carbonate

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($CaCO_3$), iron and silica are reduced and become concentrated. They form an adherent deposit on heat exchanger surface which leads to lower efficiency and finally damage of cooling system [12]. The hardness of water is harmful to the boilers as the deposition of salts occurs, which reduces the efficiency of the boiler. Hard water is safe to drink but using over a long interval of time can lead to many problems. Hard water interferes with laundering, washing, bathing and personal grooming. Clothes laundered in hard water may look dingy and harsh. Hard water utilization in the home can lead to other issues as well. The high levels of calcium and magnesium intake in humans will leads to kidney stone, diarrhoea and many other serious health problems [12].

The most common method used in the treatment of this type of power plant wastewater is the use of chemical coagulation process, which uses salts of iron and or aluminum to cause pollutant deposition. But this method will be expensive while consuming large amount of chemicals. In recent years, the electrocoagulation method alone has replaced the usual methods of stripping, activated carbon adsorption and membrane (RO) to treat this type of effluent [5,13,14].

Electric current, voltage and time are the three most important factors in determining the power or cost required in electrocoagulation [15,16]. The current passing through the wastewater determines the amount of metal ions required for coagulation. In a constant current, the voltage changes depending on the resistance of the effluent. The lower the resistance of the effluent, the lower the voltage required. Time plays an important role in calculating the required power of the process, for complete coagulation of wastes [17]. The required power is obtained from this equation:

$$P = \frac{V \cdot I \cdot t}{1000} \qquad (1)$$

where P is power consumption in kWh, V is voltage in volts, I is current in amperes and t is time in hours.

The contact surface of the electrode determines the size of the electrocoagulation set-up. The higher the contact surface of the electrodes, the greater the volume of effluent between the electrodes (assuming their gap is constant) and the greater the volume of material that coagulates. Also, the contact surface of the electrode affects the current density and the surface to volume ratio. The surface-to-volume ratio (S/V) in contact with the electrodes is an important parameter in increasing the scale and the optimal value of 15–45 m^2/m^3 has been reported. As the S/V increases, the current density decreases [18]. Current density is the ratio of current to the active surface of the electrode (A/m^2). The current density is a very important parameter as it determines the total amount of metal ions released at the anode and the density of the bubbles produced in the electrolyte and the time required for the material to coagulate. Holt states that high current densities up to 150 A/m^2 are required for processes with flotation cells or large settling tanks [18]. The current density can be easily controlled by changing the current, but for a given process, the optimum current density must be obtained by experiment [17]. The gap between the electrodes is proportional to the voltage. The shorter the gap between the electrodes, the lower the voltage required. Of course, in this case, less volume of coagulation is achieved. Several series of tests must be performed to find the optimal gap at which the maximum amount of effluent coagulates while consuming the least amount of energy. If the gap is too short, a short circuit may occur [17,19]. During EC process, pH changes by dissolution of the anode. So, pH of the effluent must be controlled because it has a significant role in achieving the desired high treatment efficiency. The pH of the effluent can be easily controlled by adding acid or base [17].

The objective of this study is to develop and optimize a pilot-scale EC system to reduce the hardness of wastewater of a power plant cooling tower. The application of electrocoagulation process for the treatment of an industrial effluent and on a semi-industrial scale is a research innovation. Experimental design is a research achievement by considering several variables and achieving the optimal range of variables along with the economic evaluation of the method. Another innovation of this research was to perform the hardness reduction process in a shorter time compared to traditional methods and since chemicals are not used in this process, it is more cost-effective and environmentally friendly. Reliability and performance and this process is much more effective and competitive compared to methods such as liming or soda ash.

2. Materials and methods

2.1. Chemicals and reagent used

The complete list of chemicals and reagents and their purity is presented in Table 1.

2.1. Wastewater specifications

The investigated wastewater is the water coming out of the cooling towers of Isfahan Power Plant. Due to the circulation in the system and the evaporation, the remaining wastewater is concentrated and its hardness increases. To reuse water, it is necessary to reduce its hardness to the standard value. The specifications of the resulting wastewater are given in Table 2.

2.2. Pilot design

The pilot design consists of the following components shown in Fig. 1. The studied pilot-scale EC system was built using polyethylene sheets with a capacity of 1 m^3/h has the dimensions of 0.8 m width, 1 m height and 1.3 m length. The arrangement of the electrodes is also shown inside the EC system (Fig. 1), including 50 pairs of U-shaped dual electrodes. The anodes and cathodes are connected together and to the positive and the negative poles of the power supply, respectively. According to Fig. 1b, a copper belt is connected to all the electrodes from the back, which transmits current from the power supply to the electrodes. The connection method and the number of plates that are connected directly to the power supply are determined according to the required voltage. For example, if the input power is 24 V and all the panels are connected directly to

Table 1
List of chemicals and reagents used

	Chemicals and reagents	Manufacturer/Purity	Chemicals and reagents	Manufacturer/Purity
1	Sulfuric acid	Merck (Germany)/98%	Phenolphthalein	Loba Chemie (India)/99%
2	NaOH	Sigma (USA)/99%	Calcium chloride	Merck (Germany)/99%
3	Ammonia	Merck (Germany)/25%	Magnesium sulfate	Merck (Germany)/99%
4	Eriochrome Black T solution	Loba Chemie (India)/99%	Hydrogen peroxide	Sigma (USA)/30%
5	Ethylenediaminetetraacetic acid	Sigma (USA)/97%	Potassium permanganate	Merck (Germany)/98%
6	Silver nitrate	Loba Chemie (Germany)/99%	Oxalic acid	Sigma (USA)/99%
7	Thiourea	PubChem (USA)/99%	KH_2PO_4	Merck (Germany)/98%
8	Ammonium purpurate	Loba Chemie (India)/Extra pure		

Table 2
Characteristics of cooling tower effluent used in this study

	Before treatment
T-hardness (mg/L)	1,430
Mg-hardness (mg/L)	520
Ca-hardness (mg/L)	910
Cl^- (mg/L)	945
Sulfate (mg/L)	960
BOD (mg/L)	2
COD (mg/L)	16.2
TSS (mg/L)	10
TDS (mg/L)	3,525
pH	7.9

the source with their screws, the applied voltage between them is 24 V, but if the screws of each part of the device (positive and negative) are connected to the device one by one, the applied voltage between them will be 12 V. Since the electrodes are corroded over time and require periodic replacement, the electrodes are made in dual modules for ease of replacement. The beginning and end pages of each section have a negative charge and are attached to the wall of the tank. The reason for this is that only the part of the pages facing each other is effective in wastewater treatment. For this reason, if a positive page uses at the beginning and end of each section; part of the plate remains unused and also, if the plate is not attached to the tank wall with a negative charge, the effluent flow that passes through the space between the plate and the wall will not be treated. For this reason, the end module of the negative pole of the device was made in triplicate

2.3. Electrocoagulation tests

In order to perform optimization tests, after experimental design, according to Table 3, the experiments were performed in the order provided by the Design-Expert software [20]. For this purpose, the initial conditions of the wastewater from the cooling tower of Isfahan power plant, such as total hardness, Ca^+ hardness, Mg^+ hardness, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), total suspended solids (TSS), Cl^- and sulphate [21] were determined. After adjusting the pH by adding sulfuric acid or sodium hydroxide according to the value provided in Table 3 for each experiment, the effluent entered the coagulation chamber. Afterward, the desired current density (Table 3) was created by adjusting the voltage value using the volume on the power supply. At the specified time, which was determined by the software for each test, the power supply was turned off. Then, samples were left for 15 min to allow clusters of suspended particles to float to the surface due to turbulence generated by the electric Samples were taken from the transparent liquid below, and the factors mentioned earlier and the efficiency of the system were measured.

2.4. Measurement of factors

2.4.1. Total hardness

50 mL of sample water was poured into flask and 1 mL ammonia buffer and 5 to 6 drop of Eriochrome Black T indicator were added. The solution turns into wine red color. The content was titrated against ethylenediaminetetraacetic acid (EDTA) solution. At the end point color changes from wine red to blue color. Based on the volume of EDTA consumed, the total hardness calculated according to Eq. (2) [22].

$$\text{Total hardness of water mg/L}\left(\text{CaCO}_3\text{ scale}\right) = \frac{\text{mL of EDTA used}\times 10^3}{\text{mL of sample}} \tag{2}$$

2.4.2. Ca^{2+} hardness

50 mL of the sample was poured into a 250 mL flask and the pH was adjusted to about 12–13 with normal sodium hydroxide. Formerly, 0.1 to 0.2 g of murexide (ammonium purpurate) added. After adding the reagent to the sample, a pink color was created. It was titrated with EDTA until the purple color appeared (end point) and the volume of EDTA consumed was obtained. The Ca^+ hardness calculated according to Eq. (3) [22].

$$\text{Calcium ion}\left(\text{mg/L}\right)\text{ in terms of calcium carbonate} = \text{mL of EDTA used}\times 10^3 / \text{mL of sample} \tag{3}$$

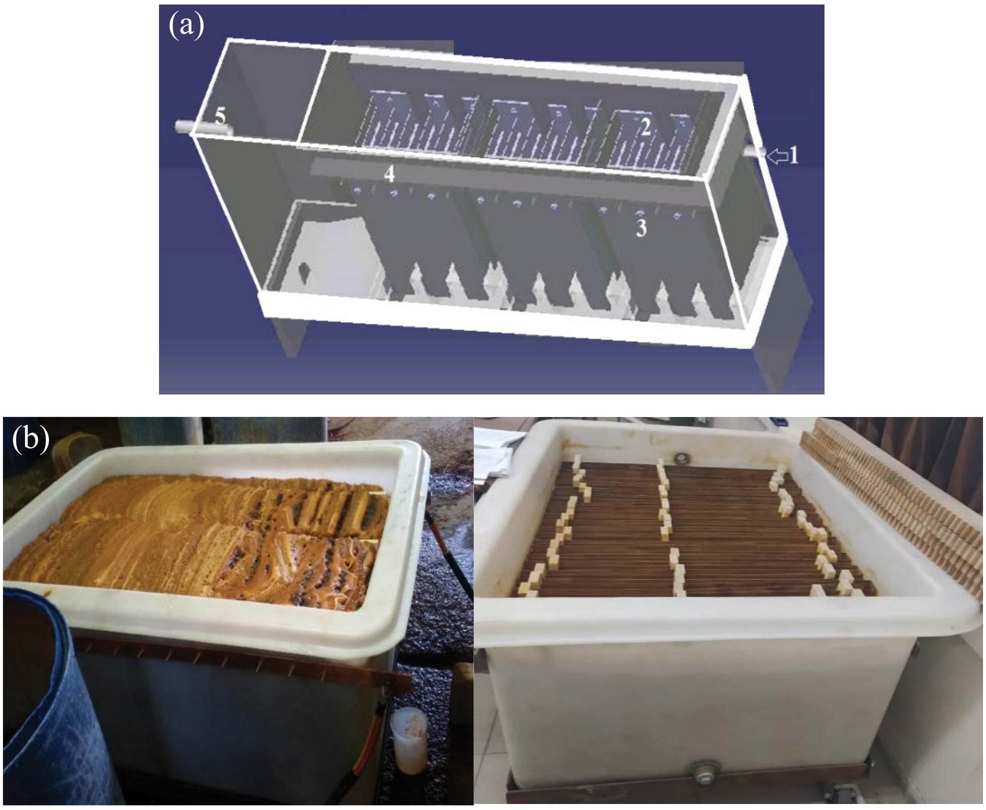

Fig. 1. (a) Configuration of the electrocoagulation system. The different sections of this design are 1: inlet; 2: electrodes; 3: brass screw; 4: copper belt; 5: outlet. (b) A view of the constructed pilot and the sludge collected on the pilot at the end of the treatment.

2.4.3. Mg^{2+} hardness

Considering that total hardness is the sum of calcium hardness and magnesium hardness, therefore, having total hardness and calcium hardness, magnesium hardness was calculated as follows [22].

$$\text{Calcium ion}\left(\text{mg/L}\right)\text{ in terms of calcium carbonate} = \frac{\text{mL of EDTA used}\times 10^{3}}{\text{mL of sample}} \tag{4}$$

2.5. Surface response method design

In the surface response method section, among the various designs provided by the Design Expert software [20], the D-optimal method can be used to optimize 1 to 30 factors and minimize the variance of the estimated coefficients for the model. It also offers fewer experiments than other surface response methods. Therefore, due to time and cost constraints, the D-optimal method was selected. Factors considered included; current intensity (5–15 A/m^2), time (5–30 min), gap between electrodes (0.5–3 cm), pH (5–9) and ratio of surface of electrodes to effluent volume (S/V 15–45 m^2/m^3) (15–45). The experiments were performed with three replications. The reason for choosing these values was the review of other results in the literature and our own previous research and screening tests performed at the laboratory level [23–26].

3. Results and discussion

To optimize the process more precisely, the response surface methodology-central composite design (RSM-CCD) method using Design-Expert software has been used. As it is clear from the data in Table 3, the highest amount of treatment is related to Experiment No. 20. The data in the table are analyzed and the results are shown in Table 4.

Table 4 shows the analysis of variance of the mentioned data. This predicted model, is quite stable and significant. Although the coefficient of variation (CV) of desired value varies depending on the research area, basically CV < 10 is very good, 10 < CV < 20 is good, 10 < CV < 20 is acceptable and CV > 30 is not acceptable.

The model considered for the above results has been identified as a quadratic model by examining R^2 and the reliability of all possible cases. The overall capability of the model is typically described by measuring the R^2 coefficient. Since the coefficient R^2 alone is not enough to confirm the model, the analysis of variance for the model is performed. In optimization experiments, P-value which is a specified number for each parameter is used to determine the effect of parameters on the process. The parameters with P-value less than 0.05 were considered to have major effect on the response value [27]. In this study, all factors had a significant effect (Table 4). The relative importance of all parameters as well as the interaction between them in the final model is presented by the impact factor of each in the model.

Table 3
Results of optimization tests

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Response 1
Run	*A*: Current density	*B*: Time	*C*: Gap	*D*: pH	*E*: S/V	Hardness removal
	A/m^2	min	cm		m^2/m^3	%
1	15	30	1	9	15	66
2	5	30	1	6	45	62
3	15	30	1	9	45	86
4	5	30	1	9	15	48
5	10	18.5	2	7.5	30	92
6	15	7	1	9	45	50
7	10	18.5	2	7.5	30	91
8	5	7	3	9	45	44
9	10	18.5	2	7.5	30	88
10	5	30	3	6	45	50
11	15	7	1	6	45	47
12	15	30	1	6	45	81
13	15	7	3	9	15	47
14	5	7	1	6	15	34
15	10	18.5	2	7.5	30	86
16	15	30	1	6	15	61
17	15	30	3	6	15	63
18	5	7	3	9	15	50
19	10	18.5	3.5	7.5	30	70
20	10	18.5	2	7.5	30	96.7
21	10	18.5	2	5.2	30	82
22	15	7	3	6	15	50
23	10	18.5	2	7.5	30	96.5
24	15	7	1	9	15	48
25	2.5	18.5	2	7.5	30	47
26	10	18.5	2	7.5	7.5	84
27	10	1.3	2	7.5	30	21
28	5	7	1	6	45	36
29	5	7	1	9	15	40
30	10	18.5	2	7.5	30	95.7
31	15	7	3	6	45	55
32	15	30	3	9	15	60.2
33	10	18.5	2	7.5	52.4	94.3
34	5	7	1	9	45	45
35	5	30	1	9	45	62
36	10	18.5	2	9.7	30	93
37	10	18.5	0.5	7.5	30	84
38	5	30	3	9	15	37
39	10	35.7	2	7.5	30	78
40	15	30	3	6	45	72
41	10	18.5	2	7.5	30	95.8
42	5	7	3	6	15	33
43	5	30	3	6	15	36
44	5	30	3	9	45	46
45	15	30	3	9	45	70
46	5	7	3	6	45	28
47	15	7	3	9	45	38
48	5	30	1	6	15	33
49	15	7	1	6	15	37
50	17.5	18.5	2	7.5	30	72

$$\begin{aligned}\text{Hardness removal} = {} & +92.09 + 7.80A + 9.22B - 2.13C + 2.07D + 3.95E + 3.85AB + 0.48AC \\ & -1.90AD + 0.15AE - 2.28BC - 0.78BD + 3.77BE - 1.53CD - 2.35CE \\ & -1.23DE - 14.18A^2 - 18.65B^2 - 6.35C^2 - 1.65D^2 - 0.92E^2 \end{aligned} \tag{5}$$

The above formula is in fact a model intended for calculating and estimating the efficiency of treatment by changing the amount of various factors. Three models of RSM including the first-order response-surface model (FO), the two-way interactions model (TWI) and the full second-order model (FSO) are usually selected to fit of data, and finally the best model is selected using analysis of variance (ANOVA). The model with higher R^2 and insignificant lack of fit will be selected as appropriate model [28,29]. FSO model with a higher R^2, and also an insignificant lack of fit [0.1194] indicated superiority than the rest.

3.1. Statistical tests and model reviews

To ensure that there were no significant errors in the laboratory data and the proposed model, a number of statistical tests were performed. The first test was to check the normal probability function of the residuals. The results of this test show (Fig. 2) that the laboratory points are located around the line, so it can be ensured that there is no abnormal term in the system error. If the pattern of points has a nonlinear state, it indicates a non-normal error.

The next test looks at the quality of the model. In this test, the predicted points are plotted using the model according to the laboratory data. In a suitable model, the resulting points are placed around the 45° line. Since the data is located around the 45° line, it can be said that the model predicts the data well to the desired extent. The graph of predicted values in terms of laboratory values related to this study is shown in Fig. 3.

3.2. Effect of pH

Fig. 4 shows the effect of initial pH on the efficiency of treatment. With increasing pH to a value between 5 and 7.5, the efficiency increases and then decreases. As can be seen, pH 7.5 is the best pH for treatment and at lower or higher pH, the amount of hardness removal decreases. This could be due to the fact that the pH is suitable for producing more aluminum hydroxide in a liquid medium at a point between 6 and 8. However, there is no significant difference between the low threshold and the high threshold and the optimum point, and the difference in efficiency is about 5%. Also, as can be seen from Table 4, the effect of this factor is very low (*F*-value: 4.47) and its significant effect is within the borderline (*P*-value: 0.0431), which indicates that the changes of this factor do not have a significant effect on the purification efficiency.

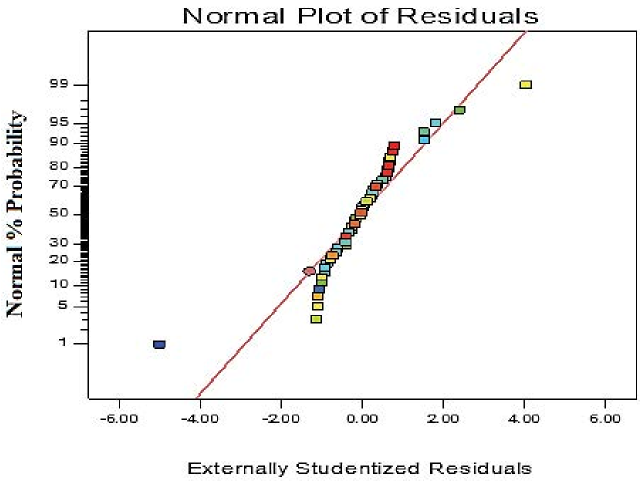

Fig. 2. Normal probability diagram of residual values.

In some studies, a pH of about 6.5 is said to be optimum [15,30]. Resan Kalash et al. [19] also investigated hardness removal using electrochemical cell. Operating parameters for the EC process such as electrode type (Al and graphite), initial pH (7–8), electric potential (10–28.5 V), electrode spacing (2–4 cm) and operating time (0–60 min) were evaluated for optimum operating conditions using batch process. Similarly, removal efficiency of 85% was obtained at pH of 7 [19]. Compared to other studies, the results are in accordance with the results of other researches [4,14,31] which also obtained pH 7–7.5 as the optimal pH for hardness removal by electrocoagulation. In some studies, higher pH is considered as optimum [17,32].

3.3. Effect of time

Fig. 5 shows the effect of time in EC process. This factor has the greatest impact on treatment. As can be seen, the slope of the diagram was steeper than the slope of the pH diagram. Efficiency increases as time increases, but it decreases after 17.5 min, which can be considered as the optimal time. When the process time increases from 7 to 17.5 min, the purification efficiency increases by about 30%. In times of less than 10 min, there is not enough time to free coagulants and form clots, so the efficiency of the process will be low. As time goes on, more metal ions are released into the effluent, and the particles have more opportunity to come into contact with the metal ions, resulting in more clots and increased removal efficiencies [30]. Also, after more than 25 min, the efficiency of the process starts to decrease, which is due to the increase in water temperature and re-dissolution of part of calcium and magnesium in water. In the time range of 17.5–25 min, the efficiency of the process remains constant, therefore, to reduce the time and cost of the process, we consider 17.5 min as the optimal time. Other studies on hardness removal using this system have suggested higher times such as 30 [4,14] and 60 min [3,19,31] for the optimal value and the result in this study is the shortest time to reach more than 85% efficiency.

3.4. Effect of current density

From Table 4, it can be seen that after time, the current density with *F*-value of 63.33 has the greatest effect

Table 4
Analysis of variance for hardness removal efficiency in response surface experiments

Source	Sum of squares	df	Mean square	*F*-value	*P*-value Prob. > *F*	
Model	23,082.80	20	1,154.14	32.92	<0.0001	Significant
A: Current density	2,220.54	1	2,220.54	63.33	<0.0001	
B: Time	3,103.42	1	3,103.42	88.51	<0.0001	
C: Gap	165.68	1	165.68	4.73	0.0380	
D: pH	156.91	1	156.91	4.47	0.0431	
E: S/V	570.14	1	570.14	16.26	0.0004	
AB	474.32	1	474.32	13.53	0.0010	
AC	7.22	1	7.22	0.21	0.6534	
AD	115.52	1	115.52	3.29	0.0799	
AE	0.72	1	0.72	0.021	0.8870	
BC	165.62	1	165.62	4.72	0.0381	
BD	19.22	1	19.22	0.55	0.4650	
BE	456.02	1	456.02	13.01	0.0012	
CD	74.42	1	74.42	2.12	0.1559	
CE	176.72	1	176.72	5.04	0.0326	
DE	48.02	1	48.02	1.37	0.2514	
A^2	2,352.91	1	2,352.91	67.10	<0.0001	
B^2	4,071.63	1	4,071.63	116.12	<0.0001	
C^2	472.08	1	472.08	13.46	0.0010	
D^2	32.03	1	32.03	0.91	0.3471	
E^2	9.83	1	9.83	0.28	0.6006	
Residual	1,016.86	29	35.06			
Lack of fit	897.45	22	40.79	2.39	0.1194	Not significant
Pure error	119.41	7	17.06			
Cor. total	24,099.66	49				
Std. dev.	5.92	*R*-squared	0.9578			
Mean	61.64	Adj. *R*-squared	0.9287			
C.V. %	9.61	Pred. *R*-squared	0.8531			
PRESS	3,539.30	Adeq. precision	17.806			

on the process. Fig. 6 shows the effect of current density. As can be seen, increasing the current density from 5 to 10 A/m^2 increases the hardness removal by about 25%, and the current density of 10 A/m^2 can be optimal. This can be explained by the fact that the amount of iron released from the anode increases with increasing of current density, according to Faraday's law [18]. Faraday's first law states that the mass separated from the electrodes is directly proportional to the amount of electricity passing through the electrodes. When iron ions increase in the environment, the surface of the coagulation contact and the number of active sites increases, which improves the accumulation of particles and formation of the clot [17,33,34]. At the current density of 10 to 12 A/m^2, the efficiency of the hardness reduction remains constant, therefore, to reduce the cost of treatment, we consider 10 A/m^2 as the optimal the optimal current density. Increasing the current intensity from 12 to 15 A/m^2 results in a 10% decrease in efficiency, which is again caused by the increase in temperature of the electrodes due to the high current intensity and, consequently, an increase in its temperature and the re-dissolution of some ions. The optimal current density was found to be in range of 20–80 mA/cm^2 in most of studies.

3.5. Effect of gap

The effect of the gap between the electrodes is similar to the graph of the effect of pH (Fig. 4), and the *F*-values (4.73) and *P*-value (0.0380) of this factor are also very close to the values reported for pH (Table 4). The efficiency changes in the low threshold and high threshold and the optimal point are less than 5%, so it is clear that the change

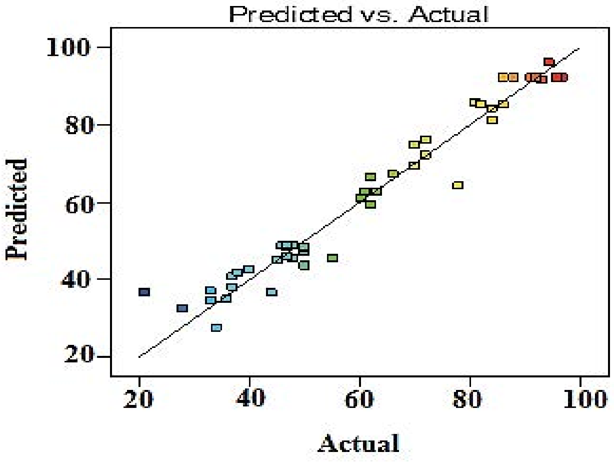

Fig. 3. Predicted values in terms of relevant laboratory values.

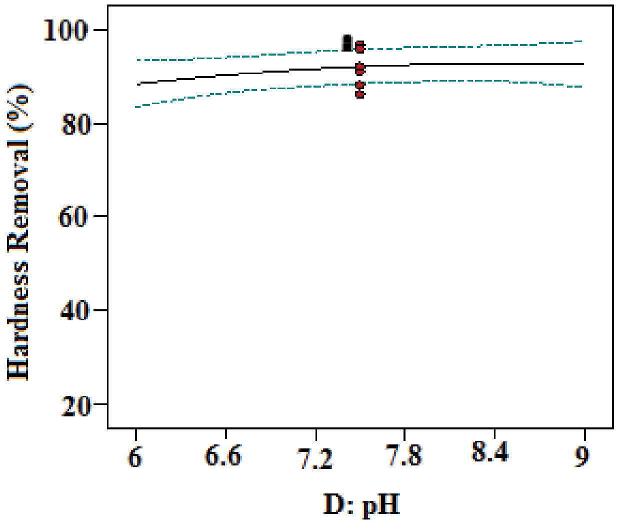

Fig. 4. Effect of pH on the efficiency of hardness removal.

in the gap between the electrodes in the investigated range does not have a significant effect on the efficiency of the process. Nevertheless, it can be understood from Fig. 7 that with the increase of the gap between the electrodes, more than 2 cm, and the slope of the decrease in efficiency becomes steeper, which shows that longer distances (more than 3 cm) can reduce the efficiency more strongly. As shown in Fig. 7, by increasing the gap between the electrodes up to 2 cm, the efficiency does not change significantly and is almost constant. Increasing the gap to more than 2 cm reduces the efficiency. This may be due to the low displacement of the ions formed during the electrocoagulation process and the less contact of the particles with the ions. The gap between the electrodes is directly related to the voltage. This means that as the gap increases, more voltage is needed to reach a certain current density. Although by increasing the gap between the electrodes, the process of electrocoagulation can be done at a larger volume, but the need for more voltage, increases the amount of energy and therefore costs. It should be noted that the gap between the electrodes interacts with another factor, which will be described below. A gap of less than 1 cm causes a high accumulation of coagulants which prevents proper flow, and formation of new clots and their transfer to the surface of the reactor. In addition, very short gaps can lead to short circuits that disrupt current transmission. Brahmi et al. [4], investigated the use of electrocoagulation with aluminum electrodes for removal of non-carbonate hardness in phosphate mining process water in Tunisian phosphate mining process water. Effects of operating

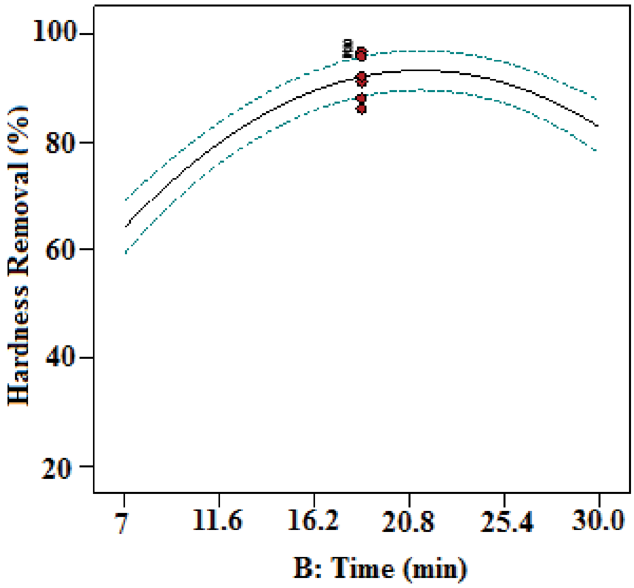

Fig. 5. Effect of time on the efficiency of hardness removal.

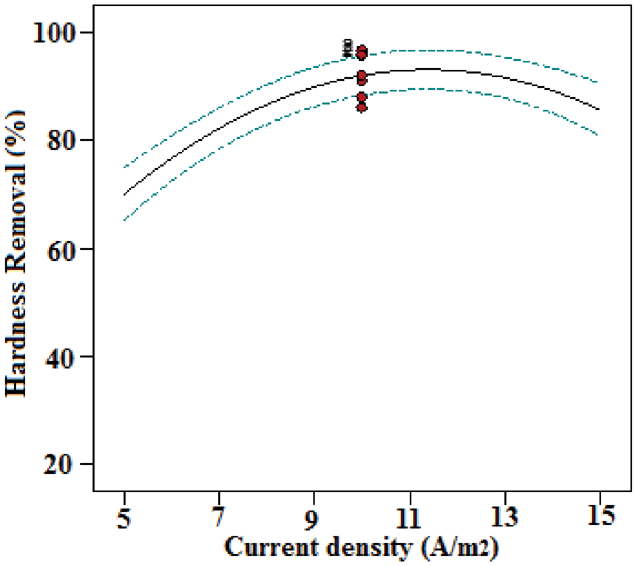

Fig. 6. Effect of current density on the efficiency of hardness removal.

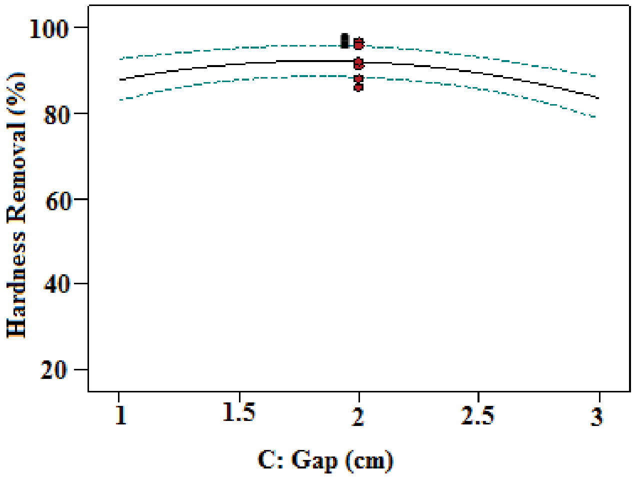

Fig. 7. Effect of gap on the efficiency of hardness removal.

parameters for the EC process such as electrode type (Al), initial pH (3–10), current density (7.4–22.2 mA/cm^2), electrode spacing (1–4 cm) and operating time (0–60 min) were evaluated for optimum operating conditions using batch process. Examination of process parameters identified optimal conditions for hardness removal at pH 7, a current density of 22.2 mA/cm^2, an interelectrode distance of 2 cm and operating time of 30 min with removal efficiency of 83.8%. A distance of 2 cm has also been proposed by other researchers as the optimal distance for removing hardness by the electrocoagulation process [19,31,35]. However, in contrast, the results of achieving optimal conditions at shorter distances have also been reported [3].

3.6. Effect of S/V

As can be seen from Fig. 8, the difference in efficiency between the minimum S/V and the maximum S/V is about 7%. However, increasing the S/V from 15 to 45 m^2/m^3 increases the hardness reduction efficiency due to the increased current density transfer and the release of coagulants. As the active surface of the electrode increases, it leads to more current transfer and production of more coagulant substances, so as can be seen in the Fig. 8, the process of increasing the efficiency with the increase of the surface is linear and incremental even up to the high threshold of the study (45 m^2/m^3). The higher the S/V, the lower the current density will be required to achieve higher efficiencies, which in turn reduces the process cost. The optimal ratio of S/V is 30 m^2/m^3. Most studies have reported ranges from 25 to 35 m^2/m^3.

Finally, the optimal point for treatment according to the results of 50 experiments is current density of 10 A/m^2, electrolysis time of 18.5 min, gap of 2 cm, pH of 7.5 and S/V of 30 m^2/m^3.

Regarding the interaction of factors, only the effect of flow intensity/time, time/gap, time/S/V, gap/S/V were significant (according to Table 4), which will be examined in the following paragraphs.

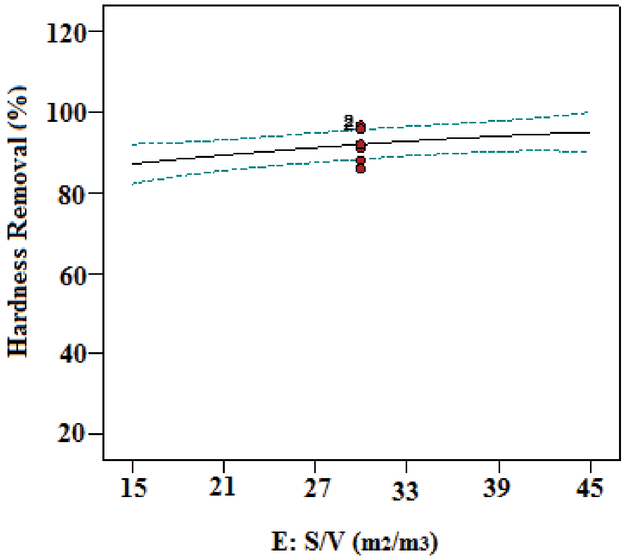

Fig. 8. Effect of S/V on the efficiency of hardness removal.

3.7. Interaction of time and current density

As can be seen in Fig. 9, the simultaneous effect of time (min) and current density (CD, A/m^2) increases the slope of the hardness removal rate. In fact, the simultaneous presence of both factors in the environment helps each other to increase hardness removal. As shown in Fig. 9, when the density is high, time has little effect on the efficiency and the changes are linear. But at low densities, as the time decreases, the efficiency decreases with a steeper slope. Since time can be controlled in experiments, but the current density is likely to change during the test, it can be concluded that higher amount of time are more appropriate, because with a change in density, the slope changes in the final response are milder and these conditions are more controllable. The two parameters were optimal in the ranges of 16.2 min < time < 20.8 min and 9 A/m^2 < CD < 11 A/m^2.

3.8. Interaction of time and gap

Fig. 10 shows the interaction of gap (cm) and time (min) on the hardness removal efficiency. In this interaction, it is observed that when the gap between the electrodes increases, the electrocoagulation time must be increased to maintain or increase the efficiency. Therefore, at a gap of 3 cm, the treatment time should be extended to 30 min to compensate for the greater gap, which leads to less current transfer. It is also observed that when the gap between the electrodes is 2cm, with increasing time, the efficiency increases with a large slope, while at a gap of 1 cm, this process is accompanied by a smoother slope. Thus, as shown in the curve of Fig. 10, the two parameters were optimal in the ranges of 2 cm < gap < 2.5 cm and 20.8 min < time < 25.4 min.

3.9. Interaction of time and S/V

Fig. 11 shows the interaction of time (min) and S/V (m^2/m^3) on the hardness removal efficiency. It is obvious

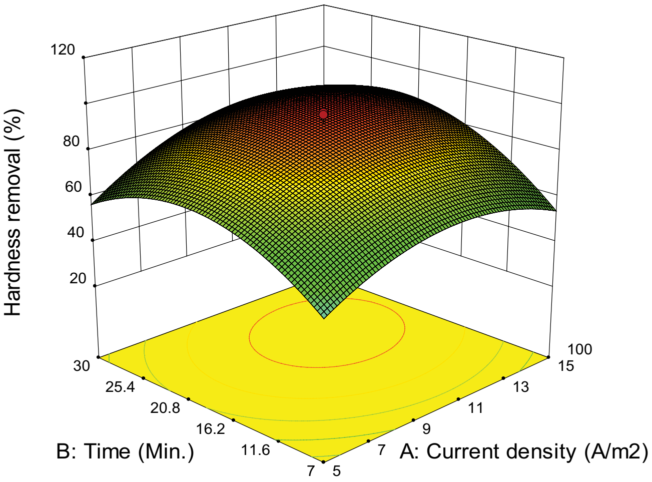

Fig. 9. Interaction of current density and time on hardness removal.

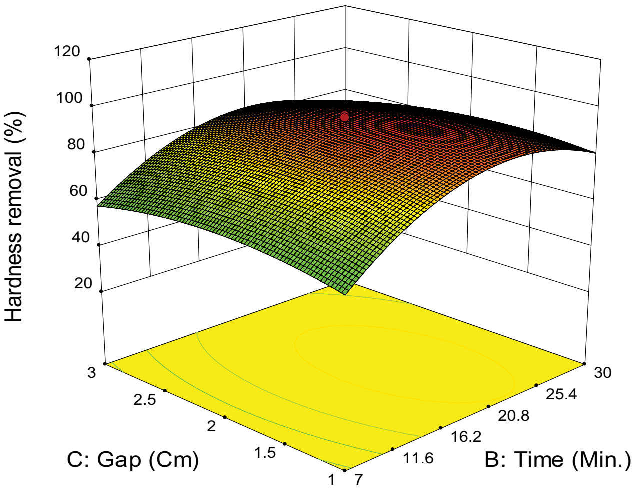

Fig. 10. Interaction of gap and time on hardness removal.

that at lower S/V ratios, more time is needed for treatment and reaching an efficiency above 80%. The more this ratio increases, less time is needed to obtain the required efficiency. It is due to when the electrodes are in contact with the effluent for a shorter period of time, the current transfer rate decreases which subsequently fewer metal ions are released. So, at low voltage and current, time must be increased to achieve the relevant efficiency. The two parameters were optimal in the ranges of 33 m^2/m^3 < S/V < 39 m^2/m^3 and 20.8 min < time < 25.4 min.

3.10. Interaction of gap and S/V

Fig. 12 shows the interaction of gap (cm) and S/V (m^2/m^3) on the hardness removal efficiency. As can be seen in the figure, the interaction between these two factors is less significant than other interactions and the curve surface is approximately flat. In other words, increasing the gap between the electrodes, increases the amount of surface area required. The two parameters were optimal in the range of 27 m^2/m^3 < S/V < 33 m^2/m^3 and 2 cm < gap < 2.5 cm.

The amount of removal of various factors in the effluent at the optimal point is given in Table 5.

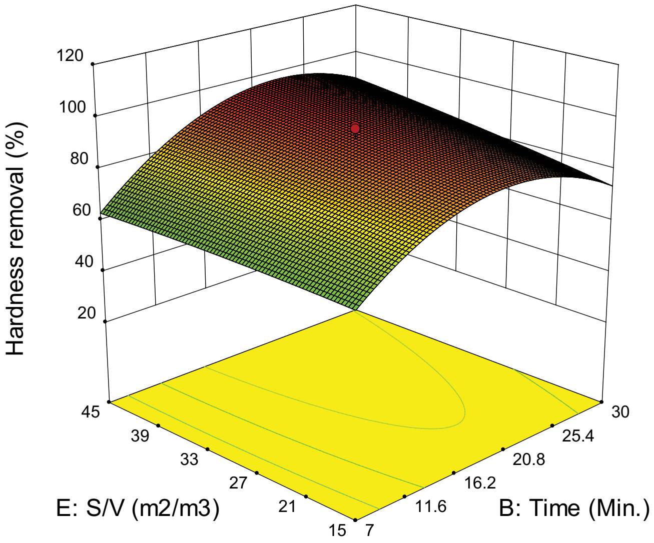

Fig. 11. Interaction of S/V and time on hardness removal.

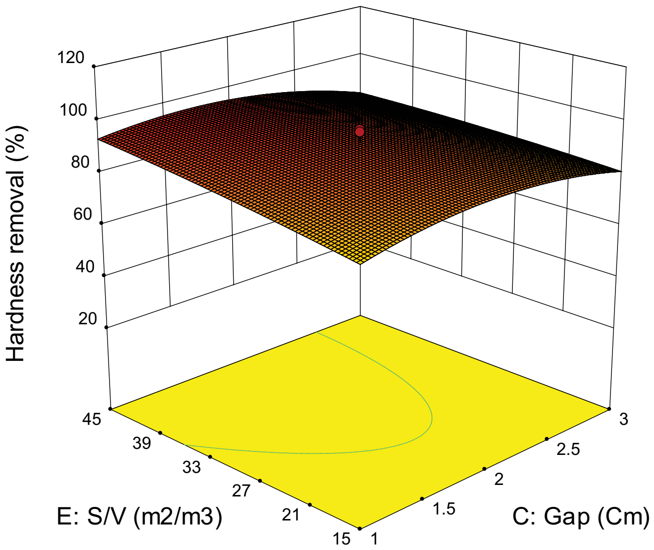

Fig. 12. Interaction of S/V and gap on hardness removal.

4. Conclusion

The results of this study indicate that the electrocoagulation method can be used for reducing the hardness of wastewater of a cooling tower with appropriate and acceptable efficiency. Other factors such as sulfate, chloride and TDS are also removed from the effluent at the same time as the hardness is removed using this process. The technology has the potential for treating highly contaminated wastewater with simple equipment, convenient

Table 5
Results of removal of various factors in the effluent at the optimal point

	T-hardness (mg/L)	Mg-hardness (mg/L)	Ca-hardness (mg/L)	Cl^- (mg/L)	Sulphate (mg/L)	BOD (mg/L)	COD (mg/L)	TSS (mg/L)	TDS (mg/L)	pH
Before treatment	1,430	520	910	945	960	2	16.2	10	3,525	7.9
After treatment	109	56	53	142	130	0	0	0	73	8.3

operation, less operating time and using no chemicals. The influence of various operational variables such as current density, time of process, pH of sample, S/V and gap between the electrodes on treatment on treatment were investigated. The optimal value obtained was the current density of 10 A/m^2, the process time of 18.5 min, the pH of 7.5, S/V of 30 m^2/m^3 and a gap of 2 cm. Furthermore, the results show that the efficiency of electrocoagulation for hardness removal is dependent on the amount of ion released by an electrode which is affected by the amount of current density. In fact, the higher the current density is, more metal ions are released and thus treatment efficiency is higher. But as a result, the cost of electricity consumption increases. Thus, the range of 9–11 A/m^2 was considered in order to have the minimum current density which causes high efficiency. Since pH has the opposite effect on the efficiency, it was maintained between 7 up to 7.8.

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References

[1] E. Ntagia, E. Fiset, L.T.C. Hong, E. Vaiopoulou, K. Rabaey, Electrochemical treatment of industrial sulfidic spent caustic streams for sulfide removal and caustic recovery, J. Hazard. Mater., 388 (2020) 121770, doi: 10.1016/j.jhazmat.2019.121770.

[2] J.N. Hakizimana, B. Gourich, C. Vial, P. Drogui, A. Oumani, J. Naja, L. Hilali, Assessment of hardness, microorganism and organic matter removal from seawater by electrocoagulation as a pretreatment of desalination by reverse osmosis, Desalination, 393 (2016) 90–101.

[3] M. Malakootian, H. Mansoorian, M. Moosazadeh, Performance evaluation of electrocoagulation process using iron-rod electrodes for removing hardness from drinking water, Desalination, 255 (2010) 67–71.

[4] K. Brahmi, W. Bouguerra, H. Belhsan, E. Elaloui, M. Loungou, Z. Tlili, B. Hamrouni, Use of electrocoagulation with aluminum electrodes to reduce hardness in Tunisian phosphate mining process water, Mine Water Environ., 35 (2016) 310–317.

[5] D. Syam Babu, T. Anantha Singh, P. Nidheesh, M. Suresh Kumar, Industrial wastewater treatment by electrocoagulation process, Sep. Sci. Technol., 55 (2020) 3195–3227.

[6] N. Esmaeilirad, K. Carlson, P.O. Ozbek, Influence of softening sequencing on electrocoagulation treatment of produced water, J. Hazard. Mater., 283 (2015) 721–729.

[7] J.U. Halpegama, K.Y. Heenkenda, Z. Wu, K.G.N. Nanayakkara, R.M.G. Rajapakse, A. Bandara, A.C. Herath, X. Chen, R. Weerasooriya, Concurrent removal of hardness and fluoride in water by monopolar electrocoagulation, J. Environ. Chem. Eng., 9 (2021) 106105, doi: 10.1016/j.jece.2021.106105.

[8] S.B. Kausley, K.S. Desai, R.A. Patil, C.P. Malhotra, A.B. Pandit, Comparative study of lime softening, soda ash process, and electrocoagulation for the removal of hardness from groundwater, Proc. Indian Natl. Sci. Acad., 88 (2022) 379–391.

[9] B. Khaled, B. Wided, H. Béchir, E. Elimame, L. Mouna, T. Zied, Investigation of electrocoagulation reactor design parameters effect on the removal of cadmium from synthetic and phosphate industrial wastewater, Arabian J. Chem., 12 (2019) 1848–1859.

[10] M. Kobya, F. Ulu, U. Gebologlu, E. Demirbas, M.S. Oncel, Treatment of potable water containing low concentration of arsenic with electrocoagulation: different connection modes and Fe–Al electrodes, Sep. Purif. Technol., 77 (2011) 283–293.

[11] M. Mahmood, N. Yasri, B. Fuladpanjeh-Hojaghan, E.P. Roberts, Influence of operating conditions on the removal of silica and hardness by continuous electrocoagulation. J. Environ. Chem. Eng., 10 (2022) 108899, doi: 10.1016/j.jece.2022.108899.

[12] P. Sengupta, Potential health impacts of hard water, Int. J. Prev. Med., 4 (2013) 866–875.

[13] P.R. Kumar, S. Chaudhari, K.C. Khilar, S.P. Mahajan, Removal of arsenic from water by electrocoagulation, Chemosphere, 55 (2004) 1245–1252.

[14] S. Zhao, G. Huang, G. Cheng, Y. Wang, H. Fu, Hardness, COD and turbidity removals from produced water by electrocoagulation pretreatment prior to reverse osmosis membranes, Desalination, 344 (2014) 454–462.

[15] J. Koren, U. Syversen, State-of-the-art electroflocculation, Filtr. Sep., 32 (1995) 153–146.

[16] B.K. Nandi, S. Patel, Effects of operational parameters on the removal of brilliant green dye from aqueous solutions by electrocoagulation, Arabian J. Chem., 10 (2017) S2961–S2968.

[17] S. Sathe, Culturing and Harvesting Marine Microalgae for the Large-Scale Production of Biodiesel, Thesis, The University of Adelaide, Australia, 2010.

[18] P.K. Holt, G.W. Barton, C.A. Mitchell, The future for electrocoagulation as a localised water treatment technology, Chemosphere, 59 (2005) 355–367.

[19] K. Resan Kalash, I.N. Ghazi, M.A. Abdul-Majeed, Hardness removal from drinking water using electrochemical cell, J. Eng. Technol., 33 (2015) 78–89.

[20] J.A. Wass, Design-Expert 5.0, Biotech Software & Internet Report, Comp. Softw. J. Sci., 1 (2000) 88–95.

[21] E.W. Rice, R.B. Baird, A.D. Eaton, L.S. Clesceri, Standard Methods for the Examination of Water and Wastewater, American Public Health Association Washington, D.C., 2012.

[22] A. Standard, Standard Test Method for Hardness in Water, Annu. B. ASTM Stand, 2002.

[23] D. Arabian, Optimization of electrocoagulation system for municipal wastewater treatment, Desal. Water Treat., 217 (2021) 145–158.

[24] D. Arabian, A. Bolhasani, S. Karamian, E. Honarvar, Design and construction of a novel electrocoagulation reactor and process optimization for petrochemical spent caustic treatment, Desal. Water Treat., 239 (2021) 150–161.

[25] H.R. Pouretedal, M. Shamsi, D. Arabiyan, Statistical optimization of nitrocellulose removal from industrial wastewater by electrocoagulation using response surface method, Desal. Water Treat., 212 (2021) 212–219.

[26] H.R. Pouretedal, M.M. Amooshahi, S. Damiri, Degradation of sulfolane in petrochemical industry wastewater by electro-Fenton treatment using response surface method, Desal. Water Treat., 254 (2022) 38–49.

[27] M.A. Bezerra, R.E. Santelli, E.P. Oliveira, L.S. Villar, L.A. Escaleira, Response surface methodology (RSM) as a tool for optimization in analytical chemistry, Talanta, 76 (2008) 965–977.

[28] A. Mohammadi, S. Nemati, M. Mosaferi, A. Abdollahnejhad, M. Almasian, A. Sheikhmohammadi, Predicting the capability of carboxymethyl cellulose-stabilized iron nanoparticles for the remediation of arsenite from water using the response surface methodology (RSM) model: modeling and optimization, J. Contam. Hydrol., 203 (2017) 85–92.

[29] H. Godini, A. Sheikhmohammadi, L. Abbaspour, R. Heydari, G.S. Khorramabadi, M. Sardar, Z. Mahmoudi, Energy consumption and photochemical degradation of imipenem/cilastatin antibiotic by process of UVC/Fe^{2+}/H_2O_2 through response surface methodology, Optik, 182 (2019) 1194–1203.

[30] S. Gao, J. Yang, J. Tian, F. Ma, G. Tu, M. Du, Electro-coagulation–flotation process for algae removal, J. Hazard. Mater., 177 (2010) 336–343.

[31] M. Malakootian, N. Yousefi, The efficiency of electrocoagulation process using aluminum electrodes in removal of hardness from water, J. Environ. Health Sci. Eng., 6 (2009) 131–136.

[32] C.T. Matos, M. Santos, B.P. Nobre, L. Gouveia, *Nannochloropsis* sp. biomass recovery by electro-coagulation for biodiesel and pigment production, Bioresour. Technol., 134 (2013) 219–226.

[33] P. Holt, G. Barton, C. Mitchell, Electrocoagulation as a Wastewater Treatment, The Third Annual Australian Environmental Engineering Research Event 1000, 1999, pp. 41–46.

[34] M. Yasasve, M. Manjusha, D. Manojj, N. Hariharan, P.S. Preethi, P. Asaithambi, N. Karmegam, M. Saravanan, Unravelling the emerging carcinogenic contaminants from industrial waste water for prospective remediation by electrocoagulation – a review, Chemosphere, 307 (2022) 136017, doi: 10.1016/j.chemosphere.2022.136017.

[35] F.Y. AlJaberi, Desalination of groundwater by electrocoagulation using a novel design of electrodes, Chem. Eng. Process. Process Intensif., 174 (2022) 108864, doi: 10.1016/j.cep.2022.108864.