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Design and construction of a novel electrocoagulation reactor and process optimization for petrochemical spent caustic treatment

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ABSTRACT

This study defines treatment of petrochemical spent caustic wastewater by electrocoagulation method. In this regards a novel and industrial reactor with a capacity of 5 m^3/h was designed and constructed. The main factors affecting this system were optimized. The factors including; current density, time and initial pH were optimized using the Design Expert Software. The ultimate goal of the optimization and response considered in the response surface tests was to reduce the amount of chemical oxygen demand (COD). The results revealed that current density of 10 A/m^2, the process time between 60 to 70 min, and the pH 9 are the optimal process conditions. Energy consumption increases with increasing the current density and time, and pH changes do not affect energy consumption. In this optimal range, the energy consumption per one cubic meter of spent caustic is between 2.6 and 2.8 kWh. The amount of COD in the optimal range reached 2,400 from 45,000 mg/L. In this COD range, the remaining contaminates in spent caustic can be treated by conventional wastewater treatment methods such as activated sludge.

Keywords: Chemical oxygen demand; Electrocoagulation; Design expert; Reactor design; Spent caustic

1. Introduction

Spent caustic is an effluent from the caustic system to remove hydrogen sulfide and mercaptan [1]. The composition of spent caustic is very toxic and fragrant. This effluent has chemical oxygen demand (COD) 10,000 to100,000 mg/L, biochemical oxygen demand (BOD) 5,000 to 50,000 mg/L, TOC 1,000 to 5,000 mg/L and sulfide 5,000 to 35,000 mg/L [1]. As can be seen, the amount of pollutants, especially COD in the effluent is very high and it is not possible to discharge or enter the effluent into conventional treatment systems such as biological systems. On the other hand, this effluent contains valuable materials such as various polymers that can be used in other industries such as paper making if recovered [2].

Spent caustic comes from a variety of sources. In these streams, sulfides and organic acids are removed from the production stream by transfer to the caustic phase. Hydrogen sulfide is used, and the produced effluent (diesel crystalline, kerosene naphthalene, jet fuel, and LPG sulfide) is usually a mixture of materials called spent caustic [3,4]. This effluent is contaminated by sulfides, carbonates, and in most cases by a variety of organic acids. Methods such as incineration, wet air oxidation, hydrogen peroxide wet oxidation, and electrocoagulation or other specialized processes are used to treat this effluent [1,3–8]. In a chemical oxidation system, which consists of a reactor in which chemical oxidation reactions occur at high temperatures and pressures and has a separator. The effluent enters the reactor with a catalyst and hydrogen peroxide and chemical

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reactions take place at high temperatures. Inside the separator, the decomposed gas and sludge are separated and the oxidized effluent is sent for neutralization and treatment. The advantage of this system is the ability to oxidize most spent caustic pollutants, but its disadvantages include very high process costs, high risk of explosion and require special attention and care (hydrogen peroxide is very corrosive and decomposes in heat) [6].

In wet air oxidation method, this system is the most common method of spent caustics treatment [5,9]. This method can treat spent caustic types at different temperatures and pressures. No by-product or excess sulfur is produced from the exhaust gas of the system. Spent caustic can be reused after this process. Spent caustic is usually treated in oxidation reactors. In this process, sulfide is converted to products such as sulfate ions. Other compounds and contaminants in Spent caustic affect WAO systems [1,5,9]. Today, the combined method of wet air oxidation with oxidizing compounds such as hydrogen peroxide and ozone is used simultaneously to reduce organic and ammonia loads [1,6]. In the process of wet oxidation with hydrogen peroxide, due to the use of hydrogen peroxide, the temperature needs to be low and the pressure of the air phenomenon can reach the atmospheric pressure. The feed pump increases the pressure of the solution to about 28 bar (400 Pa) and the solution is mixed with compressed air. The fluid is heated inside the transducer or in direct contact with steam. The hot fluid stays inside the reactor for 1 h at 200°C. Advantages of this system include all types of spent caustic can be treated, equipment are resistant to corrosion, low cost of operation and maintenance of the system. The disadvantages of this system are high energy consumption and safety issues due to high temperature and pressure [1,5,6,9].

In recent years, the method of electrocoagulation has been used to treat this type of effluent, which in all cases showed very high efficiency and low cost [7,8,10,11]. This method is the fastest treatment method of this type of effluent compared to the previous methods, especially the wet air oxidation method [8,11]. Previous systems used high amounts of chemicals and therefore produced large volumes of sludge, which is usually toxic and difficult to dispose of, but in this method no chemicals are used and less sludge is produced. This process uses two or more electrodes, usually made of iron or aluminum. The two electrodes are placed in an electrolyte medium and connected to an electric current source. At the anode electrode, which is the sacrificial electrode, iron or aluminum ions are released and hydrogen gas bubbles form around the cathode [12–14]. The advantages of this system can be fully automated for continuous operation, reducing the number of process units in the treatment plant, resulting in a sharp reduction in the required surface of the treatment plant and reducing the operating costs of the treatment system [15,16]. Due to the lack of chemical addition in this method, the amount of waste is almost equal to the same amount of the deposited materials in the separation section. Therefore, the amount of sludge resulting from this process is much less than other methods. Various factors influence this process, including; Current density or rate of electric current input: The amount of Al^{3+} and Fe^{3+} ions produced depends on the amount of electric charge applied to the electrodes. If the electric current is low, metal ions are not produced, and if the amount of electric charge is too much, it will cause current loss and also increase the temperature of the solution. [8,11]. In this research, a new electrocoagulation package with 5 m^3/h capacity has been designed and manufactured, which in addition to being portable, offers higher efficiency than the previous routine systems due to its novel design. Another innovation of this research is the simultaneous optimization of system performance and energy consumption for spent caustic wastewater treatment. In this study, treatment of petrochemical spent caustic wastewater was investigated using an electrocoagulation system and the optimal treatment conditions were determined. In this regards a novel and industrial reactor with a capacity of 5 m^3/h was designed and constructed.

2. Materials and methods

2.1. Reactor design

The reactor was designed according to Fig. 1. This reactor was built with a capacity of 5 m^3/h with dimensions of 1.1 m wide, 1.1 m high and 4.5 m long.

The device consists of three main parts. These three sections include the following

- Electrocoagulation section;
- Sedimentation and separation section;
- Collection of foams and floating materials from the top of the device;

2.1.1. Electrocoagulation section

Fig. 1 gives an overview of this section. This section consists of several parts. Each part has a set of electrodes that are spaced 0.5–2 cm apart. In Fig. 2. The arrangement of the electrodes is shown. The input solution enters each section from the bottom and after passing through the electrodes from the top, enters the next section. To separate floating and light materials from effluents; there are two nonconducting pages at the end of each section. The first page, which is also shorter, is closed from the bottom and the current only passes through it. The second plate, which is higher, is open from the bottom and the current passes only from the bottom. The arrangement of these two plates is such that the floating material remains on the water and only water free of disturbing substances passes between the two non-conducting plates and enters the next part. Floating materials also come out of the upper edges of the device. Each part of the device consists of a number of metal electrodes. These electrodes have a positive and negative charge in between. The electrodes on one side are always connected to the positive pole and the electrodes on the other side are always connected to the negative pole of the power supply. 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 the source with their screws, the applied voltage between them is 24 V, but if the screws of

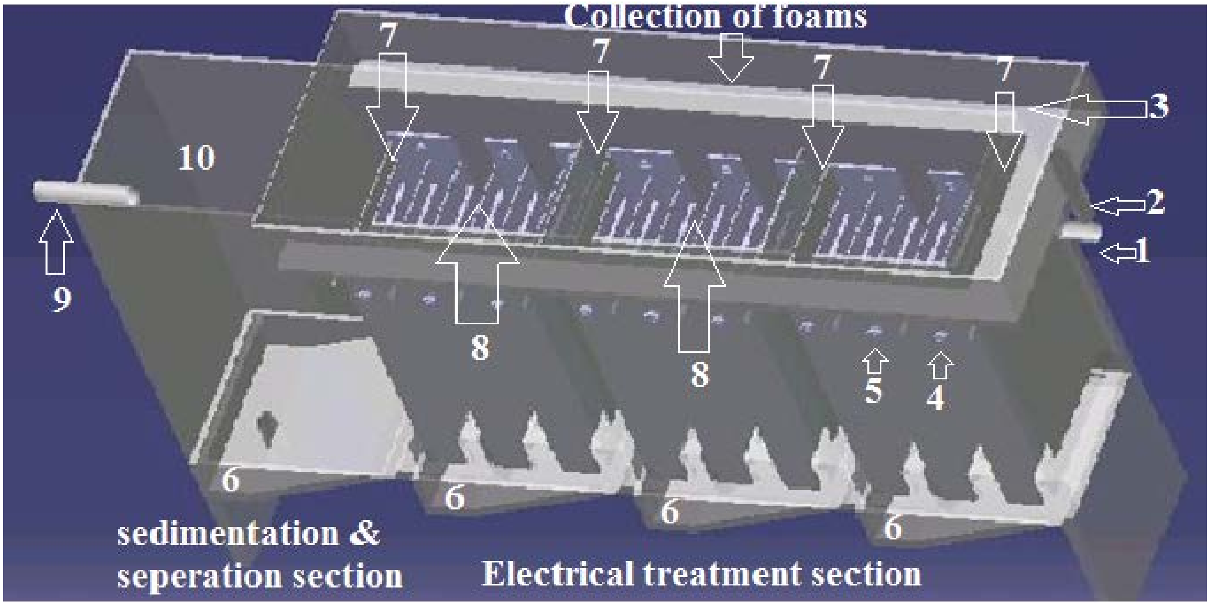

Fig. 1. The design of electrocoagulation reactor: 1. Inlet, 2. Output of floating materials, 3. Foams collecting section, 4. Anode connection screws, 5. Cathode connecting screws, 6. Decanter, 7. Nonconducting pages, 8. Electrodes, 9. Outlet, 10. Sedimentation section.

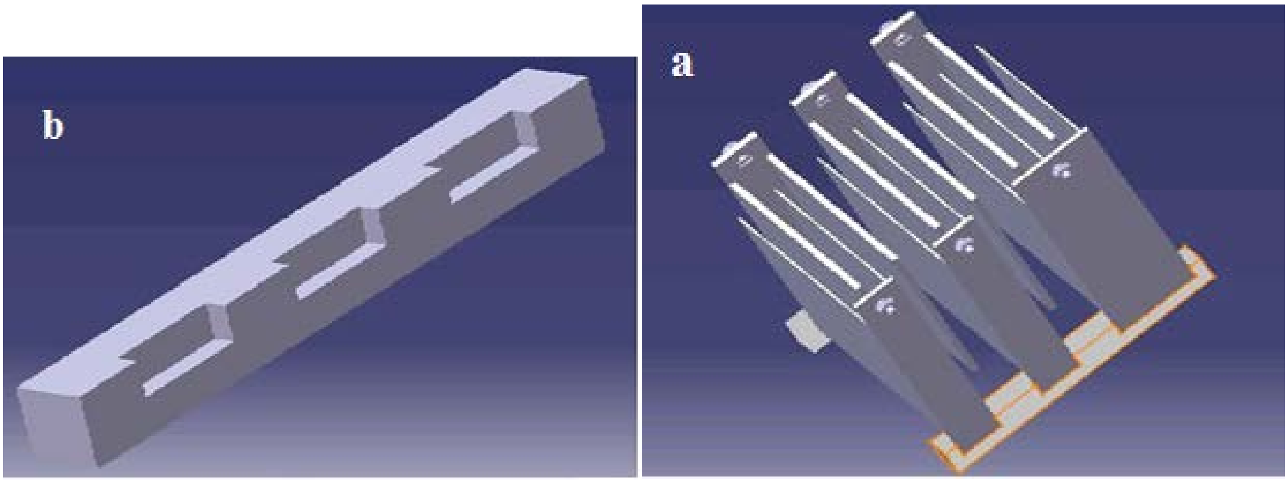

Fig. 2. The arrangement of the electrodes (a) and plastic grooves for held modules (b).

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. Fig. 2 shows the image of these modules. There is a hole in the upper part of these modules that is connected to the body of the device by a screw. The electrical connection is also established by the same screw, at the end of the module, there is also an appendage that sinks into a plastic groove (Fig. 2).

There is a decanter at the bottom of each treatment unit. To prevent the transfer of effluent flow turbulence to the sediments in the decanter and increase the efficiency of the decanters, a mesh plate is placed on top of each decanter. Fig. 3 shows the decanter as well as the mesh screen. The height of the installed electrical panels is slightly less than the height of the liquid in each section. This allows the entire length of the electrical panels to be exposed to current and consumed completely. The beginning and end pages of each section have a negative charge and are attached to the wall of the tank. In Fig. 1 this issue is quite clear. 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 (Fig. 2). The thickness of the plates used for the positive and

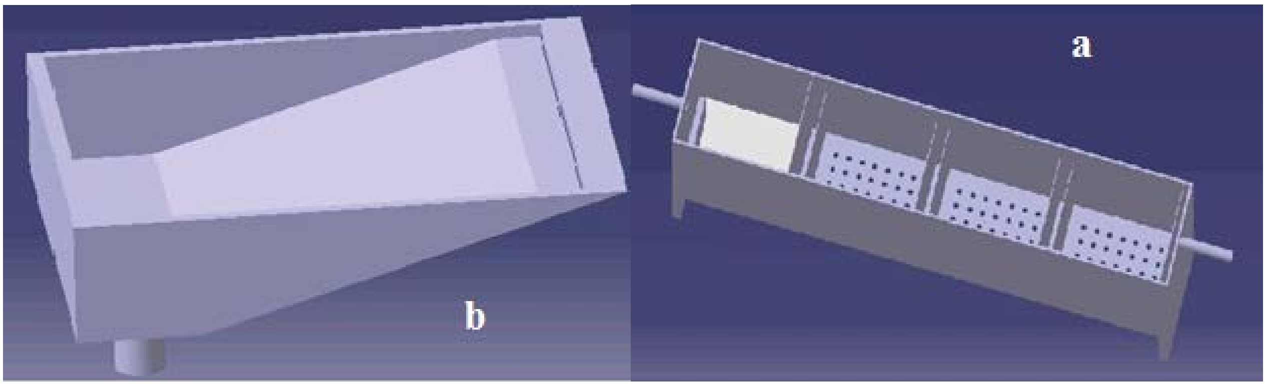

Fig. 3. Mesh screen (a) and decanter (b).

negative poles is considered different (Fig. 2) since only positively charged plates are corroded. The thickness of the positive plates is between 5–10 mm and the thickness of the negative plates is between 2–4 mm. Thicknesses higher than 10 mm for positive plates cause the distance between the plates to increase over time with the corrosion of the electrodes which increases the voltage required to supply the desired current, thus increasing the power required to treat the effluent and reduce the efficiency of the device. The height of the non-conducting plates at the end of each section is less than the previous section. This reduction in height causes the liquid to flow from one side to the other. Also, the height of the first part is less than the height of the effluent inlet and also the height of the effluent outlet is less than the height of the last part. The final built reactor with a capacity of 5 m^3/h is shown in Fig. 4.

2.1.2. Sedimentation and separation section

As shown in Fig. 1, No. 10, the settling and separation section is after the last section. The volume of this section was determined according to the inlet flow rate and the type of particles. At the bottom of this section, like the electrical parts, there is a decanter that allows the continuous exit of suspended particles.

2.1.3. Collecting foams and sludge from the top of the device

The operation of this part is such that as said before, at the end of each electrical part there are two non-conducting plates. The bottom of the first plate is closed and the bottom of the second plate is open. The height of the first plate is less than the height of the second plate. The output fluid of each section must go down the distance between the two plates in order to go to the next section. Foams and floating materials do not travel down this route due to their lower density. The height of the first and second non-conducting plates of each section is less than the height of the non-conducting plates of the next section, respectively except for the second non-conductive plate of the last part of the wastewater treatment system, which is slightly higher than the height of the tank. This reduction in height is important in two ways: the treated effluent from each section passes through the plates and enters the next section and the floating materials and foams of each section increase in diameter over time and move from the top of the device to the end of the electric treatment section. After the floating materials have exceeded a certain thickness; they overflow from the top of the package and flow into the embedded gutter and exit the gutter end pipe (Fig. 1).

2.2. Optimization of various factors in the reactor

In order to optimize different factors in the reactor, three factors of pH (7–11), current density (6–14 A/m^2) and time (40–100 min) were considered. The response surface method is a collection of mathematical and statistical techniques useful for modeling and analyzing many issues and provide a solution as a function of several variables. The purpose of this method is to optimize the response by determining the optimal range of factors that affect the process and analyzing the relationship between these factors, while minimizing the number of experiments and, consequently, spending less cost and time [17]. At this point, the DX10 software was used. In the response surface method, among the various designs that the software has provided, the D-optimal method has usability for optimization 1–30 factors, and minimizes the variance of estimated coefficients for the model. This method also provides less testing than other response-surface method.

2.3. Characterization and source of the wastewater

The wastewater used in this study was spent caustic obtained from the olefin unit of Jam Petrochemical Company, Assaluyeh, Iran. This effluent has COD 45,000 mg/L, TDS 250,000 mg/L and total suspended solids (TSS) 150 mg/L. It includes a variety of short and long chain polymers with a highly alkaline pH.

2.4. How to perform electrocoagulation test

In order to perform optimization tests, after experimental design, according to Table 1, the experiments were performed in the order provided by the software. For this purpose, the initial conditions of the wastewater, such as COD, BOD, TSS and TDS were determined. Afterwards the initial pH of the effluent was first adjusted according to the value provided in Table 1 for each experiment. For this purpose, 20 N sulfuric acid was used. A noteworthy

Fig. 4. Final reactor with 5 m^3/h capacity.

point in pH adjustment is that the use of concentrated acid, while creating large black clots, then causes a sudden drop in pH, to prevent this, different percentages of acid were tested, which 20 N sulfuric acid gave a more favorable result. Of course, thinner acids were also more suitable, since on large scale this amount of dilution would require high water consumption, so 20 N sulfuric acid was considered the optimal amount. After adjusting the pH, the effluent entered the coagulation chamber. After turning on the power supply, the desired current density (Table 1) was created by changing the voltage. After the specified time which was determined by the software for each test, the power supply was turned off. Later, samples were left for 15 min, to allow clusters of suspended particles created in the liquid due to turbulence generated by the current, to float to the surface. Samples were taken from the transparent liquid below, and the factors mentioned earlier were measured. The efficiency of eliminating of the mentioned factors were determined by obtaining the difference.

2.5. Calculation of energy consumption

To calculate the amount of energy consumed, in each test, the voltage is measured on the power supply unit. The duration is specified in minutes for all tests. The amount of current is different for different current densities and is calculated separately.

Therefore, the amount of energy consumed in kWh/m^3 of wastewater is obtained from the following equation [18]:

$$\text{Energy Consumption}\left(\frac{\text{kWh}}{\text{m}^3}\right)=\frac{10^6\times\text{time}(\text{min})\times\text{Current}(\text{A})\times\text{Voltage}(\text{V})}{1{,}000} \tag{1}$$

2.6. Cost of power consumption

Power consumption is a function of the electric current, voltage and time. In the electrocoagulation process, for an optimal current density, the voltage is controlled by the solute resistance. Given Eq. (2), the amount of cost needed to treat 1 m^3 of wastewater can be obtained from the following equation [18].

$$\frac{\$}{\text{m}^3}=\left(\frac{\$}{\text{kWh}}\right)\times\left(\frac{\text{Voltage}(\text{V})\times\text{Current}(\text{A})\times\text{time}(\text{h})}{1{,}000}\right)\times\left(\frac{1}{\text{m}^3}\right) \tag{2}$$

2.7. Cost of corrosion of the electrode

The metal content is separated from the electrode, at the certain time and the current density can be calculated by Faraday's law, according to the following equation. This equation can be expressed in simpler form, according to the following equation [18].

$$m=c\times I\times t \tag{3}$$

In this regard, m, is the mass of the abandoned metal with the gram unit, c, the electrochemical component of the metal which is a constant value for each metal and its unit is grams per ampere hour, I, is the electrical current with amperes unit and t is the time (h).

The following equation is correct, assuming that all current is spent on releasing the metal in solution. While some amount of the current is also spent on hydrogen production. The above equation is corrected as follows:

$$m=c\times I\times t\times\eta \tag{4}$$

η is the current efficiency and is expressed as a percentage. The current efficiency (η) is obtained from the following equation [18].

$$\eta=\frac{\Delta M\text{ experimental}}{\Delta M\text{ theoritical}}\times 100 \tag{5}$$

This equation is based on the comparison of the weight of the electrode that was reduced in the test and the weight of the electrode, which is reducing by Faraday's law. The theory of ΔM is obtained from the same equation. In this study, due to the ease of doing the calculations, η is considered equal to one [18].

$$\frac{\$}{\mathrm{m}(\mathrm{kg})}=\left(\frac{\$}{\mathrm{kg}}\right)\times\left(\frac{c\times I\times t}{1{,}000}\right) \tag{6}$$

3. Results

To optimize the process more precisely, the RSM-CCD section of 10 Design Expert software has been used. As it is clear from the data in Table 1, the highest amount of treatment is related to Experiment No. 14. The data in the table are analyzed with software and the results are shown in Table 2.

Table 2 shows the analysis of variance of the mentioned data. This model, as reported in its report, with F-value = 10.34, R^2 = 0.9029 and p-value less than 0.0005 is quite stable and significant. Although the Coefficient of variation 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. Adeq. Precision is equal to 10.009 and given that value over 4 is desirable, this is a sign that the model is reliable.

The model considered for the above answers 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 and is a measure of the applicability of the model. But the coefficient R^2 alone is not enough to confirm the model, hence the analysis of variance for the model is performed. The details are given in Table 2. In optimization experiments, p-value is used to determine the significant effect of parameters on the process. This value, which is specified for each parameter in the software, indicates the effect of the parameter on the system response, so if the value of this scale is less than 0.05, it indicates the significant effect of this factor on the system response [17]. In this study, all factors except pH had a significant effect and the effect of pH is only insignificant with very little deviation (Table 2). Usually, factors with a p-value greater than 0.1 are removed from the model. In this model, the parameters B (time), C (current density), with a p-value less than 0.05 are important but factor A (pH) is insignificant. 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.

$$\mathrm{COD} = +3{,}525.54 + 31.52 \times A - 380.53 \times B - 1{,}060.71 \times C - 352.00 \times AB + 16.00 \times AC + 255.00 \times BC + 334.15 \times A^2 + 245.76 \times B^2 + 490.42 \times C^2 \tag{7}$$

The above formula is in fact a model intended for calculating and estimating the amount of treatment by changing the concentration 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 [19–21]. FSO model with a higher R^2, and also an insignificant lack of fit (0.081) indicated superiority than the rest.

Table 1
Results of optimization tests

	Factor 1	Factor 2	Factor 3	Response 1	Response 2
Run	A: pH	B: Time (min)	C: CD (Current density) (A/m^2)	COD (mg/L)	Energy consumption (kWh/m^3)
1	11	100	6	4,800	2.40
2	9	70	10	3,552	2.64
3	11	40	14	4,132	2.4
4	9	70	10	3,552	2.64
5	7	40	6	6,320	0.95
6	9	70	10	3,552	2.64
7	5.6	70	10	3,704	2.64
8	9	70	10	3,552	2.64
9	11	40	6	7,100	0.95
10	11	100	14	3,364	5.59
11	9	20	10	4,316	0.8
12	12	70	10	4,312	2.64
13	7	100	6	5,940	2.40
14	9	70	17	2,400	4.48
15	7	40	14	3,800	2.4
16	7	100	14	3,928	5.59
17	9	120	10	3,200	4.8
18	9	70	10	3,552	2.62
19	9	70	3	6,100	0.79
20	9	70	10	3,552	2.61

Table 2
Analysis of variance for spent caustic treatment efficiency in response surface experiments

Source	Sum of squares	df	Mean square	*F*-value	*p*-value	
Model	2.395E+007	9	2.661E+006	10.34	0.0005	significant
A-pH	13,572.39	1	13,572.39	0.053	0.8230	
B-Time	1.978E+006	1	1.978E+006	7.68	0.0197	
C-CD (Current density)	1.537E+007	1	1.537E+007	59.67	<0.0001	
AB	9.912E+005	1	9.912E+005	3.85	0.0782	
AC	2,048.00	1	2,048.00	7.954E-003	0.9307	
BC	5.202E+005	1	5.202E+005	2.02	0.1856	
A^2	1.609E+006	1	1.609E+006	6.25	0.0315	
B^2	8.704E+005	1	8.704E+005	3.38	0.0958	
C^2	3.466E+006	1	3.466E+006	13.46	0.0043	
Residual	2.575E+006	10	2.575E+005			
Lack of fit	2.575E+006	5	5.150E+005		0.081	Not significant
Pure error	0.000	5	0.000			
Cor. total	2.653E+007	19				
Std. dev.	507.44		*R*-Squared	0.9029		
Mean	4,256.40		Adj. *R*-Squared	0.8156		
C.V. %	11.92		Adeq. Precision	10.009		
PRESS	1.966E+007					

3.1. Statistical tests and model reviews

To ensure that there are no significant errors in the laboratory data and the proposed model, a number of statistical tests were performed. The first test is to check the normal probability function of the residuals. The results of this test show (Fig. 5) 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-normality 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. 6.

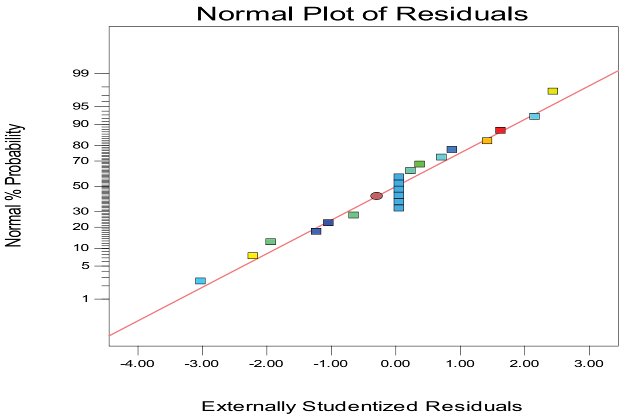

Fig. 5. Normal probability diagram of residual values.

3.2. Effect of variables

Fig. 7 shows the effect of initial pH on the efficiency of treatment. As can be seen, pH 9 is the best pH for treatment and at lower or higher pHs the amount of COD removal decreases. The result is in line with the results of Hariz et al., who also obtained pH 9 as the optimal pH for spent caustic treatment by electrocoagulation [11]. However, the effect of pH in the study area is insignificant and pH changes from 7 to 11 do not have much effect on COD removal. Aliasghari et al. also showed that pH changes have no effect on treatment efficiency [7]. In some studies, a pH of about 6.5 is said to be optimum [22,23]. In other electrochemical process like E-Fenton treatment process, also the initial pH is an important factor which can influences the overall removal efficiencies of turbidity and COD. In this regard researcher indicated that, the percentage removal of turbidity and COD were increased with increasing pH up to 7 [24].

Fig. 8 shows the effect of treatment time. As can be seen, the slope of the diagram was steeper than the slope of the pH diagram. Efficiency increases as time increases, which will be slower after 70 min, so 70 min can be considered as the optimal time. As time goes on, more metal ions are released into the liquid medium, and the particles have more opportunity to come into contact with the metal ions, resulting in more clots and increased removal efficiencies [25]. This result is in line with Shokri's study [8].

Fig. 9 shows the effect of current density. As can be seen, this factor has the greatest impact on treatment. Increasing the current density greatly increases the amount of treatment that the current density of 10–12 can be optimal.

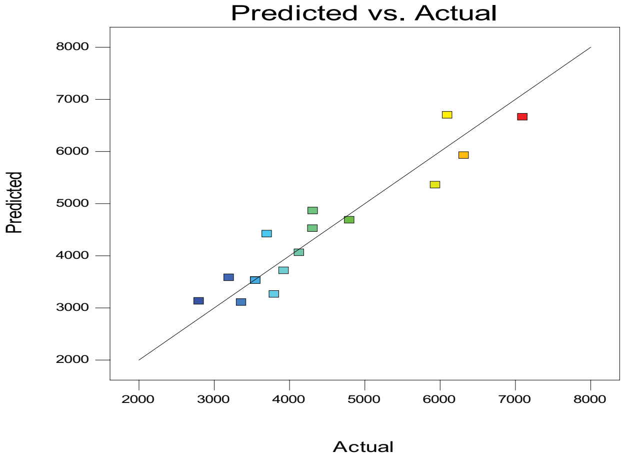

Fig. 6. Predicted values in terms of relevant laboratory values.

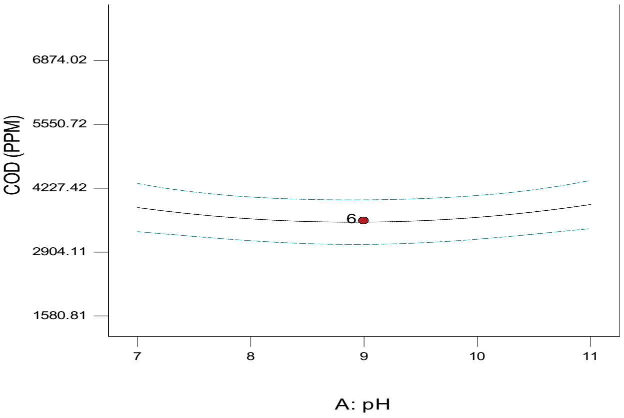

Fig. 7. Effect of pH on the efficiency of spent caustic treatment.

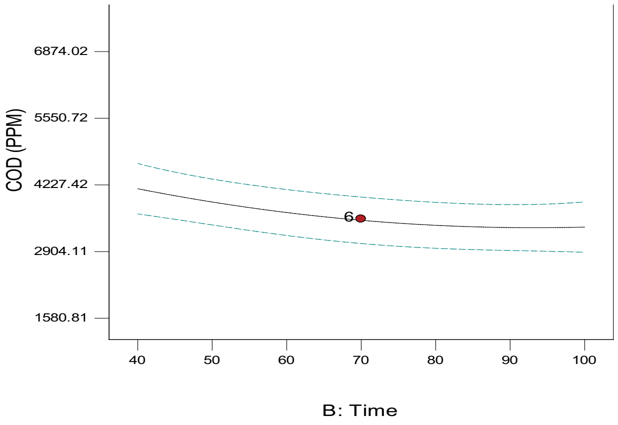

Fig. 8. Effect of time on the efficiency of spent caustic treatment.

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 [26]. 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 [22,27,28]. Also, by increasing the current density, the bubble increases and the size of the bubbles decreases, which makes the clusters float faster on the liquid surface. In total, the optimal point for treatment according to the results of 20 experiments is pH 9, time 70 min and current density 10 A.

3.3. Interaction effects of the variables

Fig. 10 shows the interaction of pH and time. In fact, this curve shows the COD removal behavior affected by both factors. According to the curve in Fig. 10, as the pH decreases at a constant current density of 10, the COD removal efficiency increases with increasing treatment time. Thus, as shown in the curve in Fig. 10, the two parameters were in the optimal range in the ranges of 10 > pH > 9 and 75 > Time > 70.

Fig. 11 shows the interaction of pH and current density on the COD removal efficiency. Reducing the pH reduces the current density required for COD removal, and at a current density of less than 10 we achieve the optimum value. This effect is achieved at a constant time of 70 min. Thus, as shown in the curve of Fig. 11, the two parameters were in the optimal range in the ranges of 9.5 > pH > 9 and 10 > CD (Current density) > 9.

As can be seen from Fig. 12, the simultaneous effect of time and current density increases the slope of the COD removal rate as compare to the single-factor mode, and this increase continues even at the highest rate. In fact, the simultaneous presence of both factors in the environment helps each other to increase the COD removal. Also, the highest amount of COD removal (Experiment No. 14) among all the factors occurs in this interaction.

3.4. Results of response surface tests for energy consumption

The amount of energy consumed was calculated for each experiment. The energy consumption of each test are given in Table 1. Table 3 shows the analysis of the variance of this response. As can be seen in Table 3, the proposed software model is a two-factorial and meaningful model. Factors whose p-value is less than 0.05 are influential factors. Current density, time, interaction of current density and time are important factors. As can be seen in the Table 3, the p-value for the model is less than 0.0001, which indicates the importance of the model. On the other hand, Adequate precision (comparison between the predicted range using the model and the average prediction error of more than 4 is desirable) is equal to 73.93 and more than 4, which is also a desirable factor for the model. The adjusted-R^2 and predicted-R^2 values are 0.9959 and 0.9850, respectively, which are in agreement. In addition, the p-value for the lack of fit equal to 0.124 indicates that this test is not significant for the model, which is desirable.

As shown in Fig. 13, energy consumption increases with increasing current density and time, which is due to increased electric current consumption. According to Chart (13-(A)), pH changes have no effect on the amount of energy consumed. In section (B), energy consumption increases with increasing time. When the time increases, the process period increases, consequently, for constant

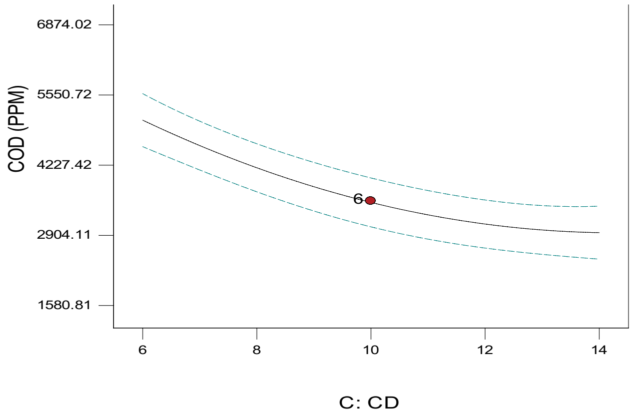

Fig. 9. The effect of current density on spent caustic treatment.

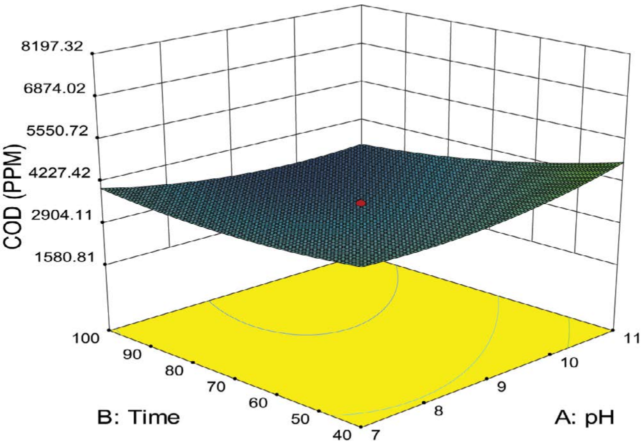

Fig. 10. Interaction of pH and time in spent caustic treatment.

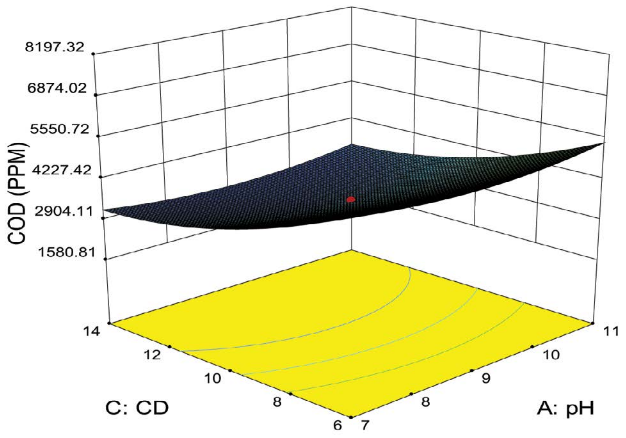

Fig. 11. Interaction of pH and current density on spent caustic treatment.

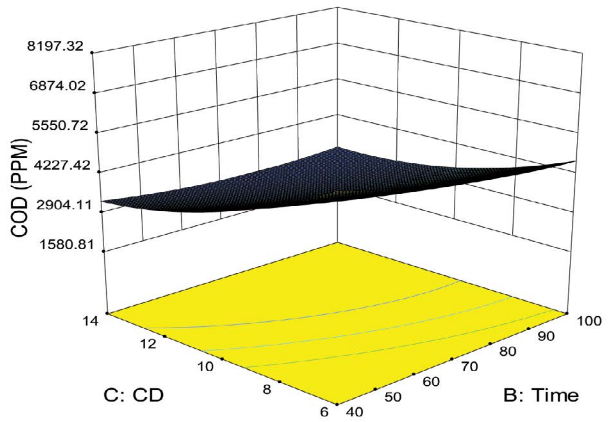

Fig. 12. Interaction of time and current density.

current density, more electrical current is consumed, and this increases the amount of energy consumed [25]. In section (C), it can be seen that increasing the current density increases energy consumption. Current density is directly related to the voltage [18]. As a result, for increasing current density, there is a need for more voltage to reach a given current density, which increases energy consumption [29,30].

According to Table 3, current density and time have significant interaction. Fig. 14 shows this interaction. The concurrent effect of time and current density increases the energy consumption. Thus, as shown in the curve of Fig. 14, the two parameters were in the optimal range in the ranges of $80 > \text{Tine} > 70$ and $11 > \text{CD} > 10$.

Finally, the optimization was achieved by maximizing COD removal and minimizing energy consumption. The energy consumption of the electrocoagulation process for spent caustic treatment in the optimal range (current density 10 A/m^2, voltage: 12 V, Time: 70 min) is 2.64 kWh/m^3. Also the initial weight of the electrodes was measured before and after all the tests. 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:

$$\begin{aligned}\text{Energy consumption} = &+ 2.59 - 3.362\text{E-}003 \times A + 1.18 \times B \\ &+ 1.13 \times C + 8.750\text{E-}003 \times AB - 0.016 \\ &\times AC + 0.45 \times BC + 0.037 \times A^2 + 0.10 \\ &\times B^2 + 0.044 \times C^2 \end{aligned} \tag{8}$$

The corrosion rate is obtained by using the electrodes for 430 min in the process. It can be said that the average corrosion rate of iron electrode is equal to 0.075 g/h. The optimal conditions of the method are according to Table 4, in which the highest removal efficiency is obtained. Hariz et al. and Shokri et al. also achieved more than 90% COD removal from spent caustic by electrocoagulation system [8,11].

The sludge collected from the sewage treatment system was analyzed for its COD and BOD, the results of which are given in Table 5.

As we can see, 28% of the initial spent caustic's BOD is found in the sludge, which can be concluded that about 72% of the BOD has been lost during the electro-oxidation process. For COD, the amount of residue in sludge is 38% which indicates the removal of 62% of the COD during the electro-oxidation process.

Table 3
Analysis of variance for the response of energy consumption

Source	Sum of squares	df	Mean value square	Prob. > *F*	*p*-value	
Model	38.28	9	4.25	519.61	<0.0001	Significant
A-pH	1.543E-004	1	1.543E-004	0.019	0.8935	
B-Time	19.07	1	19.07	2,329.56	<0.0001	
C-CD	17.40	1	17.40	2,125.94	<0.0001	
AB	6.125E-004	1	6.125E-004	0.075	0.7900	
AC	2.112E-003	1	2.112E-003	0.26	0.6225	
BC	1.63	1	1.63	199.02	<0.0001	
A^2	0.020	1	0.020	2.44	0.1493	
B^2	0.15	1	0.15	18.55	0.0015	
C^2	0.028	1	0.028	3.46	0.0927	
Residual	0.082	10	8.185E-003			
Lack of Fit	0.074	5	0.015	9.94	0.124	Not significant
Std. dev.	0.090		*R*-squared	0.9979		
Mean	2.71		Adj. *R*-squared	0.9959		
C.V. %	3.33		Pred. *R*-squared	0.9850		
PRESS	0.57		Adeq. precision	73.934		

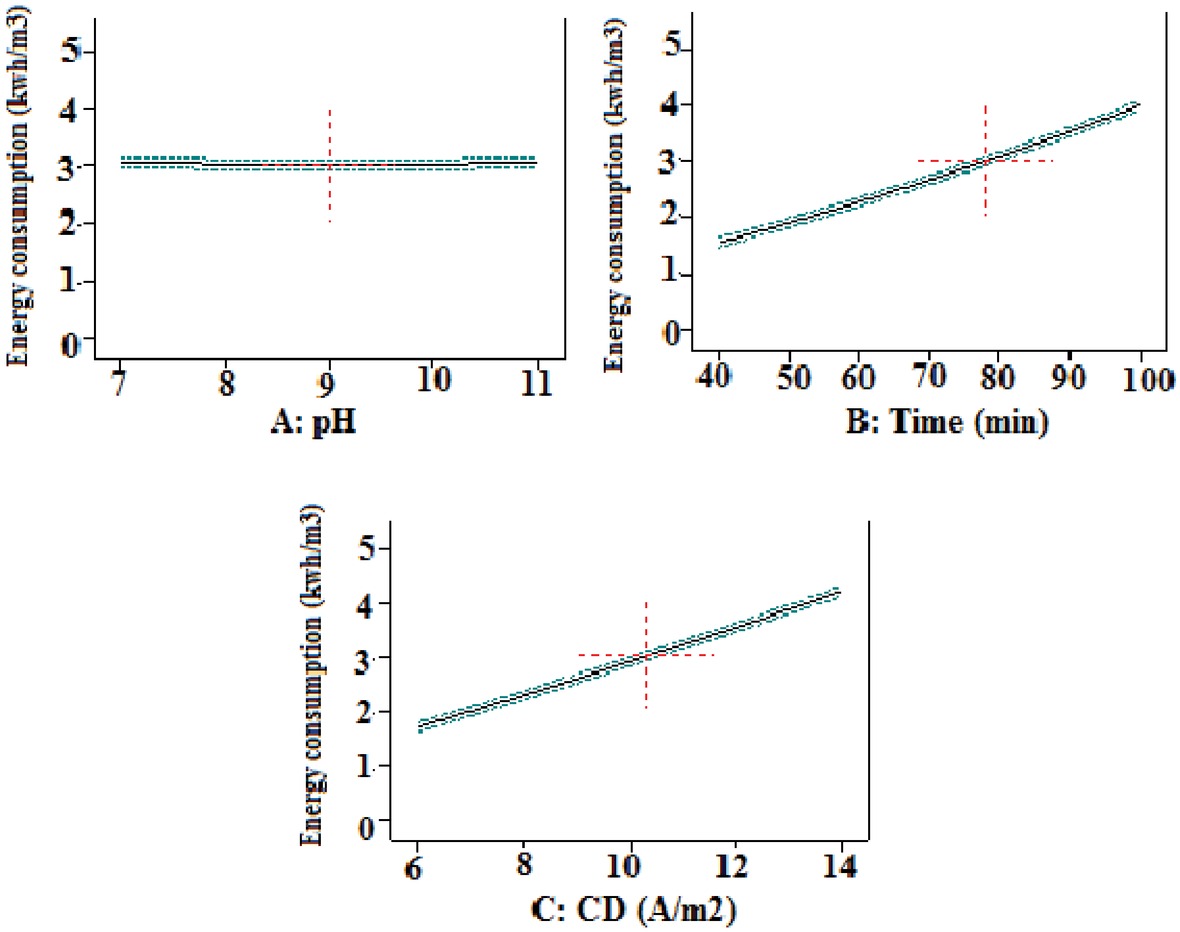

Fig. 13. Effect of different factors on energy consumption (A) effect of pH, (B) effect of time, and (C) current density effect.

Table 4
Optimal conditions of the method

Optimal condition	Inlet effluent conditions	Outlet effluent conditions
Current density: 10 A	COD: 45,000 mg/L	COD: 2,700 mg/L
Time: 70 min	TSS: 150 mg/L	TSS: 24 mg/L
pH: 9	Rate: 5 m^3/h	Rate: 4.3 m^3/h

Table 5
The amount of COD and BOD of sludge collected and compared with the initial wastewater

	Amount in sewage	Amount in sewage after treatment	Amount in sludge	Percentage remaining in sludge
BOD (mg/L)	8,200	680	2,296	28%
COD (mg/L)	45,000	2,700	17,100	38%

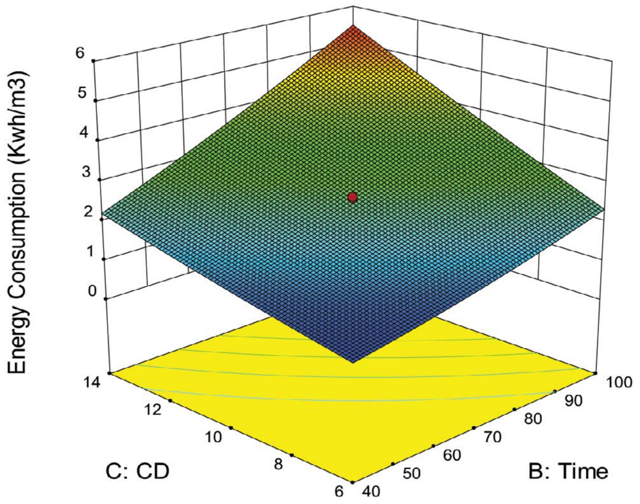

Fig. 14. Simultaneous effect of time and current density on energy consumption.

4. Conclusion

Spent Caustic is an effluent from the caustic system. The pollution rate of this effluent is very high especially COD in the effluent is in the range of 50,000–70,000 mg/L and it is not possible to discharge or enter the effluent into conventional treatment systems such as biological systems. The results of this study indicate that the electrocoagulation method can be used as an alternative and pre-treatment for spent caustic treatment so that this effluent can be acceptable for biological treatment. Due to the high pollution in this effluent, the biological treatment method is not capable of treating it because the high COD of this effluent causes a biological shock. While electrocoagulation technology has potential for treating highly contaminated wastewater such as spent caustic and is not sensitive to high pollution loads. The efficiency of electrocoagulation for spent caustic treatment dependence on voltage, current and time. The amount of voltage and current directly affect the amount of metal (iron) released. This means that, as the higher current density, the higher amount of metal ion been generated, leading to higher treatment efficiency. Increasing the time increases the chance of contact between the particles and the coagulants, which will eventually lead to a further reduction in COD. The influence of various operational variables such as current density, time and pH on treatment of spent caustic in novel reactor was investigated. The optimal value obtained was the current density of 10 A/m^2, the process time of 70 min, the pH 9. In this optimal range, the energy consumption per one cubic meter of spent caustic is between 2.6 and 2.8 kWh.

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