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The treatment of spent caustic in the wastewater of olefin units by ozonation followed by electrocoagulation process

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ABSTRACT

The ozonation and electrocoagulation (EC) process were considered as possible methods for the treatment of spent caustic in olefin units of Arak petrochemical company in Iran. At first, the COD (chemical oxygen demand) and sulfide was removed by ozonation process and the effect of temperatures, reaction time and pH were investigated on COD removal efficiency. The experiments were designed by Taguchi method. The COD was decreased from 9600 to 3030 mg/l in ozonation at optimum conditions and the sulfide was oxidized to sulfate. At a later stage, the influence of carbon dioxide injection on reduction of the pH in the real alkaline wastewater was investigated. In the final step, the residual amounts of COD and sulfide compounds are removed by EC. The effect of the electrical current density, pH and operating time were explored on the removal of COD in EC process and the optimum conditions were obtained at 40 mA/cm^2, 9 and 60 min, respectively. The COD was reduced from 3030 to 250 mg/l. At optimum conditions for COD removal, the sulfide content was reduced from 2400 to 650 mg/l in ozonation and 650 to 50 mg/l in EC process, respectively. The results showed that the ozonation followed by EC process is a good and economic technique and about 97.4% of initial COD and 97.9% of sulfide content was removed in the combined process.

Keywords: Spent caustic; Electrocoagulation; COD (chemical oxygen demand); Taguchi Method; Ozonation process

1. Introduction

One of the main units of the Arak Petrochemical Company in Iran is Olefin unit. The wastewater generated from Olefin unit is odorous and contain high sulfide, caustic soda and COD. The chemical industries generate wastewaters including non-biodegradable and toxic compounds that persist in the environment even after conventional treatment methods [1]. Sodium hydroxide solutions are usually used in the oil refining industries for the removal of Sulfur in hydrocarbon streams. In the oil industry, Caustic soda has been used for the removal of hydrogen sulfide and sulfur mixtures and the aqueous residues produced from these plants documented as spent caustic. Hence, it needs special handling and treatment before being discharged to the conventional wastewater treatment plant. These wastes are corrosive and can damage the pipes of the equipment. The large amounts of wastewater had anxieties about their harmful effects on the environment. The high COD in the wastewater of Olefin unit is originated from high sulfide compounds and salts created by the blend of sodium from the soda with hydrocarbon compounds removed from the unit. These pollutants can damage the ecological aquatic system and human health [2].

A number of efforts, based on physical-chemical methods or processes of traditional oxidation, were performed for remediation of industrial wastewater. Although the oil itself can contain sulfur, usually the treatment process is performed after the oil fraction is distilled, due to its contact with air, permitting the formation of H_2S which is very corrosive and difficult to remove [3]. In recent decades, some efforts have been made to progress better methods for the treatment of spent caustic. The possibility and benefits of a 2-step process for the biological treatment of Sulfides spent caustics under halo-alkaline conditions was explored

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by Graaff et al. [4].There are three methods for treatment of industrial wastewater comprising: physical, chemical and biological systems. However, they are non-destructive, as they only transfer pollutant from water to another phase, thus creating secondary pollution [5]. Therefore, costly operations such as regeneration of the adsorbent materials and post-treatment of solid-wastes are needed [6]. The AOPs (advanced oxidation processes) based on the ozone system have shown high efficiency in the degradation of several pollutants [7]. The ozonation treatment systems are effective for degradation of many pollutants through indirect and direct reaction mechanism. Direct ozonation that usually happens in acidic media has the benefit of high selectivity, which permits its specific use in killing microorganisms, oxidizing minerals, as well as organic contaminants [8]. In addition, one of the most important physiochemical operations employed in water treatment is coagulation, it was used for the aggregation of smaller particles into larger ones. An electric current is used via metal plates in electrocoagulation (EC) to eliminate different contaminants in water [9]. Coagulation happens upon the claim of a current, which sets the small elements in motion. EC is an active method for reducing the deposit from wastewater [10]. Though some investigation has been performed on the removal of organic pollutants in the wastewaters of oil refineries by AOPs [11], little consideration has been given to the simultaneous elimination of organic and inorganic pollutants from industrial wastes.

The Taguchi design method employs fractional factorial test designs titled orthogonal analysis (OAs) that assist to decrease the number of tests. The choice of a suitable OA is based on the level and numbers of control factors. The multiple process variables can be estimated by OA design which can affected on the performance characteristic and reducing the number of tests [12].

The aim of the present work is to find an operative treatment condition to treat spent caustic by Ozonation followed by EC. In this study, at first, the wastewater was treated by ozonation and the effect of temperatures, reaction time and pH was investigated on the residual COD. The experiments were designed by Taguchi method. The effluent from the first stage was entered to second stage for treatment by the EC and the effect of different variables such as pH, current density and operating time was explored. The efficiency of the treatment process was determined by observing the reduction of sulfide and COD. The investigation of carbon dioxide injection for pH adjustment and employing two separate processes by series for the real wastewater were the novelty of this study.

2. Materials and methods

2.1. Materials

The spent caustic wastes produced from industries vary extremely in quantity and quality. These will be determined by the nature of processed material, the various working units, and the different functioning conditions. The studied wastewater was the effluent of spent caustic from the olefin unit in the Arak Petrochemical Company of Iran, which was sampled on September 2016 with the following features (Table 1). The characteristics of spent caustic were not the same in various times and the amounts of parameters was not completely fixed. The spent caustic composition is highly variable and depends on the process condition. All studied samples were taken at one time and one point and the feedstock sample were stored in the laboratory in a cool place then it was homogenized and tested therefore the amounts of parameters in Table 1 were reported fixed.

Table 1
The approximate properties of the studied wastewater

Parameter	Amounts
Sulfide	2400 mg/l
NaOH	12000 mg/l
COD	9600 mg/l
pH	13.5
Color	Dark brown

There is a basin named as spent caustic in the company that has high sulfur and COD with high alkalinity that may cause environmental problems. It was found from preliminary experiments that ozone should be injected to the sewage at the pH lower than the actual pH of the effluent and ozone in the pH of real wastewater (pH = 13.5) had low efficiency. So, it is necessary to acidify the pH with economic methods, so carbon dioxide had been investigated for the replacement of sulfuric acid.

2.2. Experimental set-up and methods

The ozone generator was from ARDA companies of Iran and fed by pure oxygen through a gas flow meter. The outlet of the ozone generator was a mixture of O_3/O_2 that entered from the bottom of the reactor by a spongy diffuser for mixing properly, saturating the wastewater with O_3 and better mass transfer and reaction between ozone and pollutants (Fig. 1). The concentration of gaseous ozone was estimated by the iodometric technique via 2% neutral buffered potassium iodide for ozone trapping and sodium thiosulfate as a titrant. About 1500 ml of the wastewater containing definite spent caustic was mixed with ozone completely in the reactor. At regular time intervals, the samples were withdrawn and tested for analysis of COD. The obtained data were reliable. The temperature was regulated by water bath, BW20G model from a Korean company.

The output of the ozonation process was sent to the second stage for treatment by EC method. For this purpose, 1500 ml of ozonized sample was placed in a rectangular glass reactor that was constantly stirred and the aluminum plates were inserted in it. The temperature was fixed at 25°C by circulating water in the jacket of the reactor. Three anodes and three cathodes were made from aluminum plates (99.5% purity), with dimensions of 4.6 cm × 5.5 cm × 0.3 cm and connected to a digital DC power supply (Topward 6306D, 30 V and 6 A) in mono polar mode. The total immersed and effective surface area of each electrode was 42 cm^2 and the spacing between the electrodes was 1.5 cm (Fig. 2). After each run, the electrodes were cleaned and washed by HCl. The system was connected to a DC power source to provide the required current and finally the factors affecting the removal of COD were investigated.

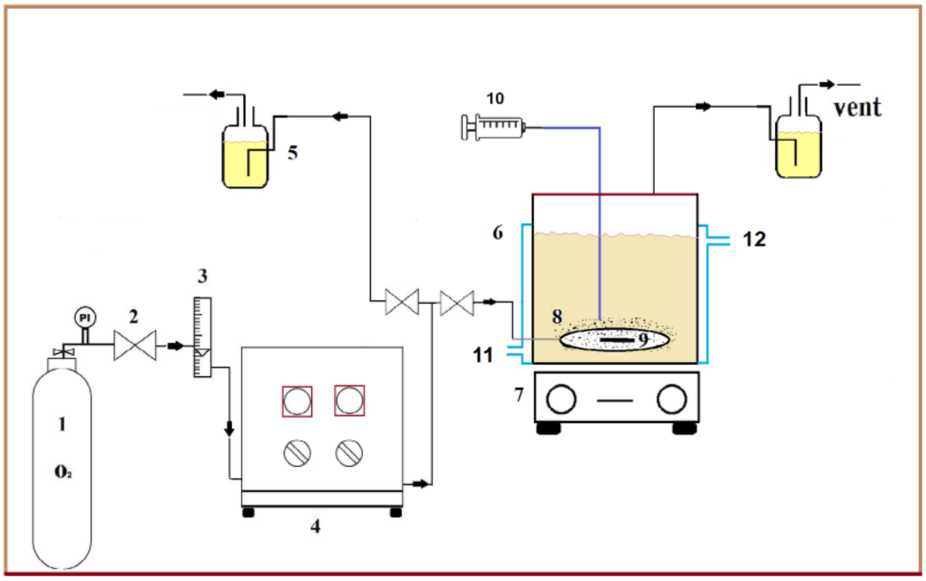

Fig. 1. Schematic diagram of the laboratory scale used. 1) pure oxygen 2) needle valve, 3) rotameter, 4) ozone generator, 5) KI solution (2% wt), 6) semi batch reactor, 7) stirrer, 8) ozone diffuser, 9) magnetic bar, 10) sampling system, 11&12) cooling water inlet and outlet from the reactor jacket to the thermobath.

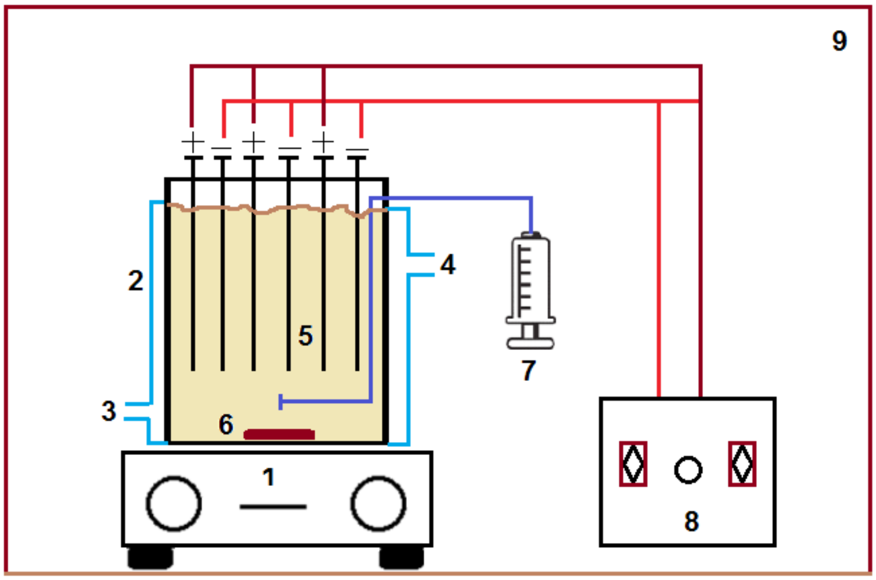

Fig. 2. Schematic diagram of electrochemical reactor used in laboratory scale. (1) magnetic stirrer, (2) batch EC reactor, (3) cooling water supply, (4) cooling water return, (5) aluminum electrodes, (6) magnetic bar, (7) sampling port, (8) DC power supply, (9) wooden box.

To measure the progress of the remediation, samples of 3 ml were taken from the reactor at times and filtered to separate sludge produced during electrolysis. In both ozonation and EC process, the factors affecting the removal of COD were optimized by Taguchi methods and in these optimum conditions the removal of sulfide was calculated. In the treatment process, the sulfide pollutants were converted to sulfate and the remaining concentrations of sulfides were measured by automatic titration of sulfide (titroprocesseur Metrohom Titrando 809) using $AgNO_3$ solution for achieving the corresponding end points. The end point of titration was noticeable by the creation of a black precipitate (Ag_2S). The titration reaction was as the following Eqs. (1)–(2):

$$Na_2S + 2Ag^+ \rightarrow Ag_2S + 2Na^+ \quad (1)$$

$$NaRS + Ag^+ \rightarrow AgSR + Na^+ \quad (2)$$

The COD content was originated from both organic and inorganic compounds (such as sulfides) in the spent caustic. The COD of samples were determined by the HACH's COD method using a COD reactor. The COD was measured by the standard closed reflux and colorimetric method [13] and the absorbance of samples for COD test was estimated by a spectrophotometer (Agilent 5443) at 600 nm. The pH was adjusted by using NaOH or HCl (0.1 M) and calculated by pH meter PT-10P Sartorius Instrument Germany.

Many tests were executed in order to determine the efficiency of the system in the degradation of sulfide and COD. The percentage of sulfide and COD removal was determined as follows Eqs. (3), (4):

$$\text{Removal of sulfide}(\%) = \left(\frac{[\text{sulfide}]_0 - [\text{sulfide}]}{[\text{sulfide}]_0}\right) \times 100 \qquad (3)$$

$$\text{Removal of } COD(\%) = \left(\frac{[COD]_0 - [COD]}{[COD]_0}\right) \times 100 \qquad (4)$$

where $[\text{sulfide}]_0$ and $[\text{COD}]_0$ are the concentration of the sulfide and amount of COD at the start of the treatment process and [sulfide] and [COD] are the concentration of the sulfide and amount of COD at a determined time, respectively. The samples were filtered by Watman 0.45 µm to eliminate the flock and meddling materials. The residual sulfate after ozonation and EC processes was determined by the turbidimetric technique by UV-spectrophotometer (Rayleigh UV 9200, China) at 420 nm [14].

Table 2
Designed experiments by Taguchi method in the ozonation process

Run number	pH	Temperature (°C)	Time	COD (mg/lit)	Predicted mean for COD
1	5	15	30	4500	4500
2	5	25	45	4100	3987.5
3	5	35	60	4000	4025
4	5	45	75	4200	4287.5
5	9	15	45	3550	3575
6	9	25	30	3750	3837.5
7	9	35	75	3400	3300
8	9	45	60	3950	3937.5
9	11	15	60	3850	3937.5
10	11	25	75	3500	3625
11	11	35	30	4800	4687.5
12	11	45	45	4850	4750
13	13.5	15	75	4650	4537.5
14	13.5	25	60	4700	4600
15	13.5	35	45	4900	5087.5
16	13.5	45	30	5900	5925
Optimum condition	9	25	75	3030	3037.5

3. Results and discussion

3.1. Ozonation process

The flowrate of O_3/O_2 mixture was 0.5 L min^{-1}, having an ozone concentration of 20.8 mg l^{-1}. The amount of ozone consumed was not studied in this project [7]. The change in the color of the wastewater was happened after 15 min of remediation. In ozonation process, the variables were pH, temperature and time. The response was the amounts of COD remained in the wastewater. The Minitab17 software was used for design of experiments. A Sixteen experiment in different operational condition was proposed by Taguchi method that is presented in Table 2. The Taguchi technique can apply for the independent assessment of factors with a small number of trials. This method contains experimental data transformation to a signal-to-noise (S/N) ratio that is a measure of the response variations that are present. The term signal denotes the quality characteristic but the term noise is a degree of the variability of the characteristics. The (S/N) ratio is based on the standard for the quality characteristics to be optimized. The "smaller is better" ratio is presented as the following Eq. (5):

$$S/N = -10\log_{10}\left(\frac{1}{n}\sum_{i=1}^{n} Y_i^2\right) \qquad (5)$$

where Y_i is the experimental response and n is the number of test in the experimental, was used because a low remained of COD was required [15,16].

The COD content in the spent caustic was measured in different conditions. The responses were fed to software and finally the result of software was analyzed. The results from Taguchi method are shown in Fig. 3.

The diagrams in Fig. 3 are designed according to signal to noise ratio and obtained from data analyze in the software.

The accuracy of the Taguchi method is demonstrated in Fig. 4, which compares the measured remaining COD against the predicted response. It can be revealed from the figure that the predictions are suitably matched with the experimental data and the R^2 was 0.978.

3.1.1. Effect of pH on ozonation

As can be seen from Fig. 3, the decomposition of ozone in aqueous solution depends on pH harshly, and it increases by rising in pH. The experiments were performed at pH of 5, 9, 11, and 13.5. At a pH of 5, the formation of hydroxyl radicals was very low, so radical reactions were minor, but direct molecular ozonolysis were highly superior and the ozone molecules was reacted with pollutant directly. At a pH of 9, the concentration of hydroxide ion was high and the production of hydroxyl radicals was very high, in another word, hydroxyl radicals were strong oxidant formed from the reaction of hydroxide ions with ozone at alkaline pH and it was initiated the chain oxidation reaction of ozone, which was non-selective and very fast [17]. The self-decomposition of ozone would be faster at high concentration of hydroxide ions and more hydroxyl radicals made at alkaline pHs, which were strong oxidizing agents than molecular ozone [18]. At very high pH (pH = 13.5), the generation of hydroxyl radicals was very high, so radicals were reacted with each other instead of pollutant molecules such as sulfides and

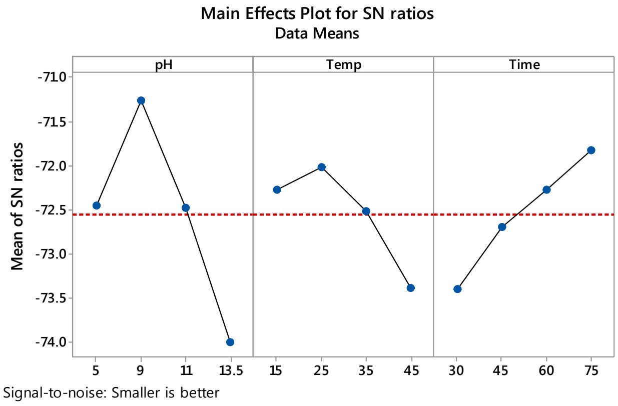

Fig. 3. Diagram of pH, temperature and time versus signal to noise in the ozonation process.

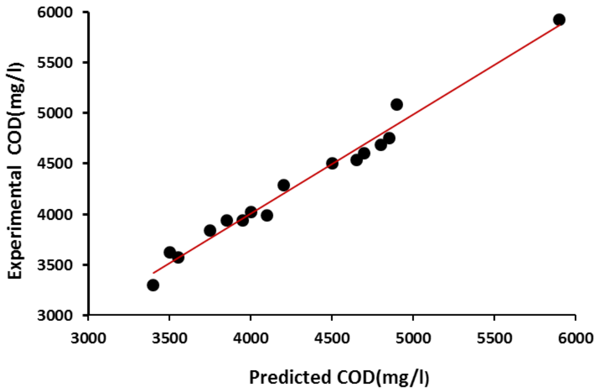

Fig. 4. Evaluation of predicted value and experimental amounts of remaining COD in ozonation process.

so on. Therefore, the pH of 9 was selected as an optimum. Comparable results were attained in the ozonation of phenol [19], and textile dyes [20] by other researchers. At high pH, the production of hydroxyl radicals is simplified by the reaction of O_3 with hydroxyl ions [Eqs. (6)–(10)] [21]:

$$O_3 + OH^- \rightarrow HO_2^{\bullet} + O_2^{-\bullet} \tag{6}$$

$$HO_2^{\bullet} + O_3 \rightarrow OH^{\bullet} + 2O_2 \tag{7}$$

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \tag{8}$$

$$HO_2^- + O_3 \rightarrow HO_2 + O_3^{-\bullet} \tag{9}$$

$$OH^{\bullet} + O_3^{-\bullet} \rightarrow OH^- + O_3 \tag{10}$$

3.1.2. Effect of temperature on ozonation

The effect of temperature on the removal of COD by ozonation was investigated from 15°C to 45°C that was in the range of wastewater temperature of the plant. Based on the Law of Arrehenius, the activation energy of reaction was decreased at high temperature and the rate of treatment process was increased. In addition, the collision between the reagents and the rate constant of reaction were increased. So, as it can be seen from Fig. 3, the removal of COD (COD remained in the solution) was increased from 15 to 25°C. In addition, the solubility of a matter depends on the chemical and physical possessions of the solvent and solute. However, the increase in temperature can result in the reduction of the solubility and residence time of ozone and subsequent decrease in the concentration of hydroxyl radicals in the aqueous phase. Similar findings were obtained previously by other researchers [22]. A mild reaction temperature of 25°C can hasten the spent caustic degradation rate or COD removal and the higher temperatures, from 25°C to 45°C, will affect on the stability as well as solubility of O_3 in the wastewater, and the COD removal rate was decreased.

3.1.3. Effect of time on ozonation

By an increase in reaction time the removal of COD was increased, so 75 min of reaction had the maximum removal efficiency and it was selected as an optimum time. As it can be seen from Fig. 3, with progress in the reaction the COD content of the wastewater was reduced, but at the final of the reaction the rate of COD removal was decreased because the generated intermediate products were resistant.

Among studied factors such as pH, temperature and reaction time, pH was the main affecting factor and its optimum amount was at 9. Secondary the time was important variable and its optimum was at 25°C. The Ozonation that was performed at pH of 9, temperature at 25°C and reaction time of 75 min, its COD content was 3030 mg/l. These conditions were introduced as an optimum. In aqueous solution, ozone reacts with sulfide ions to produce sulfate ions [23] that they have not COD. The optimization of variables for sulfide removal cannot be included in this project. The acceptable discharge limits of sulfate are higher than sulfide. The ozonation system has no residuals that can interfere on the EC process.

The contour plot of initial pH and temperature is shown in Fig. 5. It was apparent that an increase in pH from 5 to 9 can lead to the increase in COD removal efficiency, but at the more alkaline condition the removal of COD was decreased. The effect of temperature on ozonation process is clear in Fig. 5 and the results are in agreement with those of Fig. 3.

3.2. Injection of carbon dioxide into the solution for adjusting pH

Due to the fact that pH control and its reduction to optimum amounts (pH = 9) is very costly and requiring chemical consumption in industrial scale, therefore the effect of carbon dioxide injection into effluent for controlling pH was investigated in a laboratory scale. By expanding it into an industrial form, it could help the economy of the wastewater treatment process. In this stage, 1500 ml of the wastewater with the specification as mentioned in Table 1 was poured in a semi batch reactor (batch for wastewater and continuous for the carbon dioxide) employed in ozonation process and carbon dioxide was injected into the solution through a diffuser with the flow rate of 0.25 l/min. The electrode of pH meter was positioned inside the reactor and pH

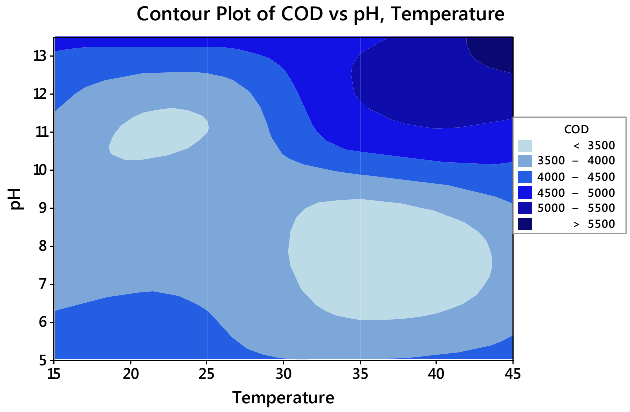

Fig. 5. Contour plots describing the remaining amounts of COD as a function of initial pH and temperature.

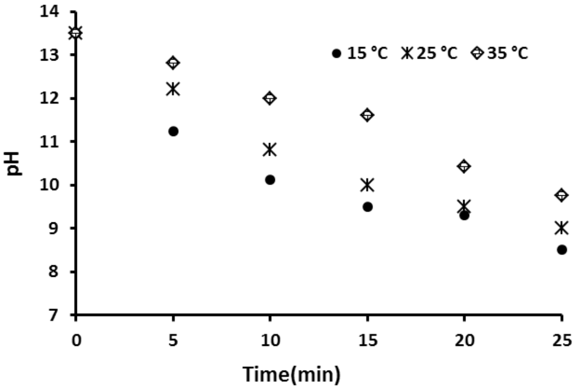

Fig. 6. Reduction of pH in Carbon dioxide injection process at different temperatures.

was controlled continuously and it was dropped gradually by injecting carbon dioxide.

The carbonic acid was formed in the solution and the color of the solution was changed from brown to green gradually. Carbon dioxide has the following reaction in the studied wastewater [Eqs. (11)–(15)] and according to the resulting reaction the pH can be dropped.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \tag{11}$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \tag{12}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{13}$$

$$CO_2 + NaOH \leftrightarrow NaHCO_3 \tag{14}$$

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \tag{15}$$

The advantages of carbon dioxide are as follows: it is cheaper than sulfuric acid and safe, in addition about 15% of the flare content of the Arak Petrochemical Company is carbon dioxide and it can be separated and recycled into the system. Carbon dioxide can control the pH better because the injection of carbon dioxide can be stopped at any pH, the piping cost is very low and carbon dioxide can be used on site.

3.3.1. Factors affecting the injection of carbon dioxide to the solution

In this section, the main parameters such as temperature and time for reduction of pH were investigated. As it can be seen from Fig. 6, carbon dioxide was injected into the solution at different temperatures (15°C, 25 and 35°C).

When carbon dioxide is used to control the pH, it must be transmitted from gas phase to liquid phase. The most important variable that influences mass transfer is the concentration of dissolved carbon dioxide. According to the above diagram the best temperature was obtained at 15°C, because the solubility and residence time of carbon dioxide molecules were decreased with an increase in temperature, subsequently the time needed to decrease in pH was reduced with decrease in temperature. The reduction of temperature to 15°C is a cost consuming method. The economics of the process should be considered, therefore in carbon dioxide injection process, time at 25 min and temperature at 25°C were chosen as an optimum condition. The pH was reduced from 13.5 to 9 in the mentioned conditions and the rest of the experiments were performed in these conditions.

In ozonation process, the bicarbonate and carbonate is an inhibitor that can hinder the radical chain reaction and even reform the molecular ozone [Eqs, (16)–(18)] [24].

$$HCO_3^- + OH^{\bullet} \rightarrow CO_3^{-\bullet} + H_2O \tag{16}$$

$$CO_3^{2-} + OH^{\bullet} \rightarrow CO_3^{-\bullet} + OH^- \tag{17}$$

$$CO_3^{-\bullet} + O_3^{-\bullet} \rightarrow CO_3^{2-} + O_3 \tag{18}$$

The buffer capacity of bicarbonate and carbonate can prevent from an increase in the alkalinity to some extent and both of them are radical scavengers and hinder the efficiency of hydroxyl radicals. But, at high pH and high amounts of hydroxide ions (originated from NaOH in this project), large amounts of hydroxyl radicals were produced from ozone reaction and hydroxyl radicals react with each other instead of pollutant [25]. So, carbon dioxide was used to quench hydroxyl radicals from being very high and prevent from scavenging effects.

3.3. Electrocoagulation expriments

The outlet of Ozonation system with the specification as presented in Table 3 was fed to the EC stage. A part of COD was originated from sulfide compounds. The sulfate was produced from the oxidation of sulfides in ozonation process. The residual sulfide, organic pollutants, and sulfate compounds from previous stage were treated by EC process. The EC includes cathode and anode electrodes. The anode is oxidized and misses electrons, while the water is reduced and obtain electrons, so the treatment of the spent caustic was improved. When the anode has contacted with

Table 3
Sample specification in electrocoagulation stage

Parameter	Amounts
Sulfide	650 mg/l
COD	3030 mg/l
pH	9
Color	a little turbid

the wastewater, the metal is released into the solution and the particles are neutralized through hydroxide complexes generation. The hydroxide complexes can be the basis of agglomerates and they are separated at the bottom of the reactor [26]. The reaction mechanism of the electrode at the anode and cathode are as follows [Eqs. (19), (20)] and it has been described by many researchers [27].

$$\text{Anode: Al} \rightarrow \text{Al}^{3+} + 3e^{-} \tag{19}$$

$$\text{Cathode: } 3\text{H}_2\text{O} + 3e^{-} \rightarrow 3\text{OH}^{-} + 3/2\ \text{H}_2 \tag{20}$$

In addition as presented by S.H. Ammar et al., [28], the concurrent evolution of hydrogen at the cathode helps the pollutant removal by floatation.

The effectiveness of EC is affected by the composition of wastewater, pH, current density and type, size and number of electrodes and configuration of metals. One of the most benefits of EC process is that no additive is needed. A Sixteen experiment in different condition was suggested by Taguchi method that is shown in Table 4.

The prediction of the removal of COD using the Taguchi method by the EC process has been compared with experimental values in Fig. 8. It can be discovered from the figure that the predictions are acceptably matched with the experimental data and the R^2 was 0.99.

3.3.1. Effect of current density

A current density was varied from 10 to 40 mA/cm^2 to study its effect on the COD removal efficiency. The current density is a critical parameter that controls the performance of the process, since it determines the dosage of coagulant rate. The remained COD content for typical EC runs were explored. As it can be seen from Fig. 7, with an increase in current density from 10 to 40 mA/cm^2, the removal efficiency of COD was increased. The reason can be explained by the increase in the production of coagulant and generation of bubbles at high current density. When the current density was increased the dissolution of the electrodes was increased in accordance with the Faraday law and the production of the small hydrogen bubbles was improved [29].

Table 4
Designed experiments by Taguchi method in EC process

Experiment number	Current density (mA/cm^2)	pH	Time	COD (mg/lit)	Predicted mean for COD
1	10	5	15	2000	2117.5
2	10	7	30	1450	1393
3	10	9	45	1100	1062.5
4	10	11	60	1170	1147.5
5	20	5	30	1050	1052
6	20	7	15	1750	1738
7	20	9	60	560	572.5
8	20	11	45	820	868
9	30	5	45	550	497
10	30	7	60	370	398
11	30	9	15	1250	1223
12	30	11	30	630	683
13	40	5	60	430	412.5
14	40	7	45	480	522
15	40	9	30	460	512
16	40	11	15	1510	1433
Optimum condition	40	9	60	250	247

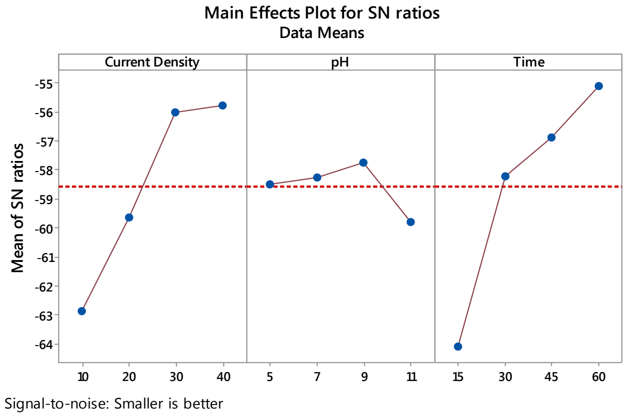

Fig. 7. Diagram of current density, pH, and time versus signal to noise in EC process.

In addition, the main effect of increasing current density is the higher rate of anode dissolution that can increase the dosage of metal ions in the solution, which subsequently improves the COD removal efficiency [30]. The aluminum hydroxide was reacted with the pollutants and they were separated at the bottom of the electrocoagulation reactor. Moreover, the sulfide and sulfate compounds can be trapped in the porous metal oxide/hydroxide precipitates [31,32]. It is clear from Fig. 7 that the differences between the current density of 30 and 40 mA/cm^2 was very low.

3.3.2. Effect of pH on COD removal

The pH is a main factor affecting the performance of the EC method [33]. The pH of the solution changes during the operating process and this change is influenced by the type of electrode material and initial pH [34]. The pH is an important factor in the solubility of aluminum sulfate and COD removal efficiency. The influence of the initial pH on the COD removal was estimated by changing the initial pH from 5 to 11 by means of HCl or NaOH (0.1 M). The results

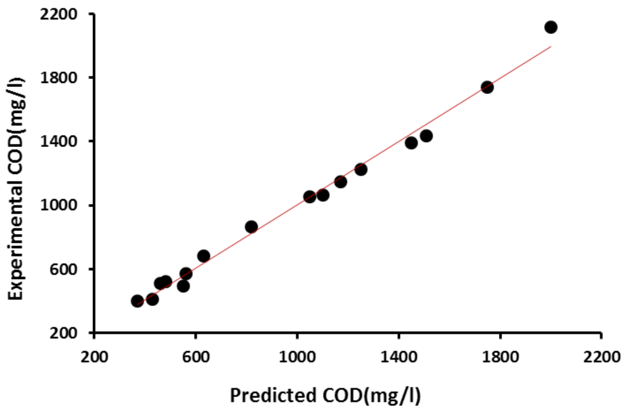

Fig. 8. Comparison of predicted value with amounts of remaining COD in EC process.

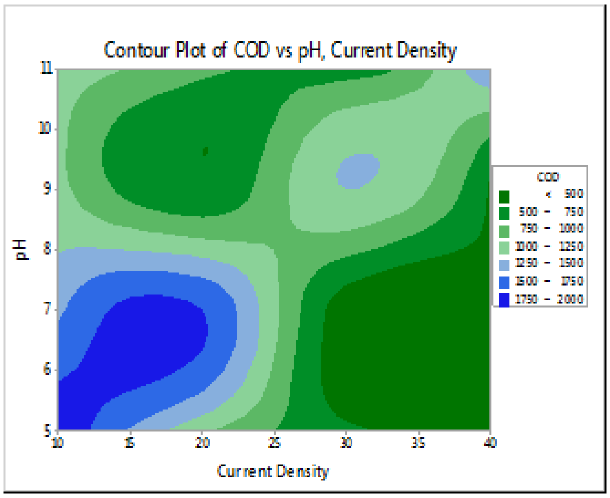

Fig. 9. Contour plots describing the remaining COD of wastewater as a function of initial pH and current density.

Table 5
Final analysis of the treated wastewater after Ozonation and EC processes

Parameter	Amounts
Sulfide	50 mg/l
COD	250 mg/l
pH	9.2
Color	Colorless

in Fig. 7, showed that the optimum pH for the reduction of COD was found to be about 9. The following reaction (Eq. (21)) was occurring in alkaline pH.

$$2Al_{(s)} + 6H_2O_{(l)} \rightarrow 2Al(OH)_{3(s)} + 3H_{2(g)} \quad (21)$$

The solubility of aluminum sulfate was increased with decrease in pH. The concentration of was increased at low pH, which reacts with the sulfate to produce. By increasing the pH from 5 to 9 the removal efficiency of COD was increased. The solubility of $Al(OH)_3$ has been stated to be at least in the pH range from 6 to 8 [35]. The aluminum hydroxide in the solid state is responsible for the removal of COD through coagulation and co-precipitation. The low and very high pH values do not favor the precipitation and the best pH was found to be 9 in this work. One of the benefits of this process is that after electrocoagulation remediation, the pH of the solution would rise for acidic effluents but drop for alkaline ones. The increase of pH at acidic condition was attributed to the hydrogen production at the cathodes [Eq. (20)] [36]. In addition, hydrogen evolution,the creation of $Al(OH)_3$ near the anode would relief H^+ leading to drop of pH. Also, there is an oxygen evolution reaction leading to decrease in pH.

3.3.3. *Effect of operating time*

The effect of residence time on COD removal efficiency was illustrated in Fig. 7. By an increase in the operating time from 15 to 60 min the removal of COD was enhanced. In EC process, the destabilization and aggregation were occurred. The destabilization is usually short, but aggregation is relatively long. Metal ions are formed at the anode through electrochemical reactions and acts as destabilization agents. At short time of reaction the concentration of Al^{3+} ions was found to be low enough to destabilize all colloidal and tiny suspended particles. Therefore the COD removal efficiencies were not significant [37,38].

The results were revealed that the maximum removal efficiency of COD was achieved in 60 min of reaction. At the high treatment time, the removal of COD was not increased sharply because the conductivity of effluent was decreased. Based on these results, the highest amount of COD is removed at the beginning of the experiment (30 min) and as time passes, the removal efficiency was not significant according to the decrease in the electric conductivity of wastewater. So, about 1 g of NaCl was added to increase the electric conductivity. It should be noted that the interference of chloride should be removed in COD test.

The contour plot of initial pH and current density is presented in Fig. 9. As it is clear, an increase in current density lead to the enhancement of COD removal efficiency, but both increase and decrease in pH can cause the remaining COD to be increased. So, it was observed that high removal of COD was occurred at a pH of 9. The results of this figure are in promise with those of Fig. 7.

The sulfate ions may also be trapped in the porous of Aluminum hydroxide precipitate. The sulfide pollutants were removed in the form of metal sulfide in the presence of aluminum anode. The residual of sulfate after EC treatment was about 400 mg/L. One of the problems of EC process is that the Sulfate reduction from the outlet of ozonation process does not appear in the form of COD loss. Because ion sulfates does not have COD. The characteristic of the wastewater after passing two stages of treatment (Ozonation and EC) was presented in Table 5. Also the COD content was reduced from 3030 to 250 mg/L. The treated wastewater can be used for the green space in the company. The removal of sulfide was performed at optimum conditions obtained for the removal of COD in Electrocoagulation and the sulfide was decreased from 650 to 50 mg/l.

It was also revealed from Table 5 that the decrease of sulfides was accompanied by a decrease of COD. The remaining COD is due to the remaining non-sulfide compounds which could be mainly intermediate hydro carbonic compounds.

Many of the previous studies used the simultaneous use of the process of ozonation and electrocoagulation, but in this project, two separate reactors were used so that the output of the ozonation process enters the EC process. By comparing the amount and efficiency of removing the sulfide and COD of this process with previous work done by other researchers [39,40], the importance of the sequential and separate use of the process is determined. It was found that combined process by series was more effective than conventional electrocoagulation and ozonation.

The ozone-electrochemical process displays the best removal rate, less energy intake which results in the lower operational cost, making it an attractive alternative for the treatment of persistent pollutants [41].

4. Conclusion

In this study the ozonation and EC processes were used by series for the treatment of spent caustic in Olefin unit. The experiments were designed by Taguchi Method and the following results were achieved:

In ozonation process, the effect of temperatures, reaction time and pH was investigated on COD removal. The optimum conditions were obtained at 25°C, 75 min and pH at 9, respectively. At these conditions, the COD was decreased from 9600 mg/l to 3030 mg/l and the sulfide was reduced from 2400 to 650 mg/l. The sulfide was oxidized to sulfate.

At a later stage, the effect of carbon dioxide injection into effluent for controlling pH was investigated in a laboratory scale. By expanding it into an industrial form, it could help the economy of the wastewater treatment process.

The pretreated wastewater by ozonation was fed to the EC process and the residual amounts of sulfide, sulfate and COD were removed. The effect of the electrical current density, pH and operating time were studied on the removal of COD. The optimum conditions were obtained at 40 mA/cm^2, 9 and 60 min, respectively. The COD was reduced from 3030 to 250 mg/l and the sulfide was decreased from 650 to 50 mg/l. The treated wastewater can be used in the green space in the company.

The results showed that the EC followed by ozonation process is a good technique for treatment of spent caustic and after 135 min of reaction about 97.4 and 97.9% of the initial COD and sulfide content was removed, respectively. In order to reach the required level of treatment with low investment cost and low cost of exploitation, the AOPs are commonly paired with other treatment approaches. The cost of this process is associated with the cost of electric current.

The optimization of influencing factors on sulfide and sulfate removal in both processes and types of electrodes in EC process can be considered as future works.

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