Degradation of sulfolane in petrochemical industry wastewater by electro-Fenton treatment using response surface method

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ABSTRACT

In this research, electro-Fenton method was used for removal and degradation of sulfolane in a petrochemical wastewater. It was selected as candidate because high solubility in water, chemical and thermal stability, low volatility and its difficult treatment. It was demonstrated that electro-Fenton method was carried out in a batch electrolytic reactor for degradation more than 97.5% sulfolane at time 60 min. The effect of operating conditions including current density, H_2O_2 dosage and pH of sample on the efficiency of process was investigated using response surface method. It was found the optimized conditions were current density 15 mA cm^{-2}, H_2O_2 dosage 3% (v/v) and pH 2.5, although the pH has the most effect on removal efficiency. Furthermore, the consumption of energy, iron electrodes consumption, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) removal and the amount of sludge produced during the application of this method were evaluated at optimum conditions. The COD and BOD removal were 55% and 43%, respectively. The degradation pathway of sulfolane by electro-Fenton as well as the transformation products was investigated using GC-FID, GC-MS, GC-SCD and total sulfur analyzer. The results demonstrated that the electro-Fenton was a feasible technique for degradation of sulfolane contaminated petrochemical wastewater.

Keywords: Sulfolane; electro-Fenton; Removal; Treatment; Industrial wastewater

1. Introduction

In today's world, the challenge of water scarcity is a serious challenge to which human beings need special attention to it. To compensate for water consumption, water purification and removal of contaminants is very important. Large industries, which are among the most consumed water resources, are always looking for a way to treatment the resulting effluent with the lowest cost and highest efficiency. Among large industries, petrochemical industry is one of the most water consuming industries. In the petrochemical industry, different organic compounds are used in large quantities to perform various chemical processes.

Sulfolane ($C_4H_8O_2S$) is an organic compound that widely used in purification of butadiene, aromatics extraction and natural gas sweetening process. Sulfolane has high stability and polarity and so it can be easily mixed with water. On the other hand, due to low vapor pressure and high boiling point, it is not easily eliminated from aqueous solutions [1–3]. Excessive consumption of this substance in the petrochemical industry has made the treatment of wastewater containing sulfolane a serious problem [4]. Therefore, several studies have been conducted to provide efficient and effective methods in wastewater treatment of sulfolane.

Due to the mentioned properties for this material, its separation from water and wastewater is difficult. The use

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of natural and synthetic adsorbents, conventional filters and membranes to separate this material is very limited. Therefore, in most researches, methods are followed for degradation of sulfolane [5,6].

Various physical, chemical and biochemical methods have been proposed for the degradation of a pollutant in a water and or wastewater [7]. Among the mentioned methods, chemical degradation has been considered due to its lower cost and greater availability. Also, among the effective chemical methods, advanced oxidation processes (AOPs) have received much attention today [7]. In these methods powerful oxidants such as hydroxyl radicals ($^•$OH) are produced and used to attack and degradation of pollutant molecules.

The importance of advanced oxidation process has led to research with subject of degradation of sulfolane that can be mentioned to Fenton's reagent [8], pressurized ozone [9], UV/O_3, $UV/O_3/H_2O_2$, UV/TiO_2, $UV/S_2O_8^{2-}$, $UV/S_2O_8^{2-}/O_3$, O_3/CaO_2 and O_3/CaO [6,10–12]. Sulfolane degradation took place relatively rapidly and with good efficiency in these processes [13,14].

However, the use of ozone gas and UV radiation imposes limitations such as challenging in production of O_3, the effectiveness of UV radiation in clear samples, high cost and its difficult application in the industry. Therefore, the use of other AOPs such as Fenton's method can remove these limitations. Perhaps the most important limitation of the Fenton method is the production reaction rate of the hydroxyl radical. To overcome this limitation, the use of hybrid methods such as electrochemical methods along with Fenton method is recommended.

In Fenton reaction, radical species of $^•$OH and $HO_2^•$ are produced in reactions of (1) and (2). Radical species react with pollutant molecules and cause them to change chemically. The degradation process is non-selective and effective [15,16]. Also, the final products are the non-harmful destructive reactions [17].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^•OH \tag{1}$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2^• + H^+ \tag{2}$$
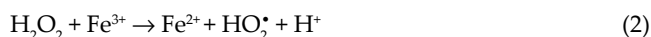
As mentioned, an electrochemical technique can be used in addition to the Fenton process. The combined method here is called the electro-Fenton (EF) method. In this method, Fenton's oxidation and electrocoagulation (EC) are performed together. Therefore, the combined method will have the advantages of both methods [18,19].

In EF method, ferrous ion and H_2O_2 can be produced through electrochemicaly using sacrificial anode and an oxygen sparging cathode. Also, H_2O_2 can be externally injected while a sacrificial iron anode is applied as a ferrous ion source. In some cases, ferrous ion is externally injected and H_2O_2 is generated using an oxygen sparging cathode. Addition of H_2O_2 and ferrous ions as Fenton's reagents are also reported to produce hydroxyl radicals in an electrolytic cell. In these conditions, ferrous ions are recreated by reducing ferric ions on the surface of cathode during the process [20,21].

In this study, the hydrogen peroxide is externally applied while a sacrificial iron anode is utilized as ferrous

ion source. Therefore, Fe^{2+} ions are produced from the sacrificial anodes and can also be re-produced by reducing Fe^{3+} at the cathode. As a result, the efficiency of the method will increase. On the other hand, H_2O_2 is added from outside and then hydroxyl radical as a powerful oxidizing agent is produced. It should be noted that, hydroxyl radical is electrochemically produced by the reaction of H_2O_2 and Fe^{2+} ion at acidic conditions. To stop it, a neutral pH is needed by adding a base compound such as NaOH. But, an important advantage of EF method is change of pH from acidic to neutral because of producing hydroxyl ion during the process and Fenton's reactions are quenched without adding sodium hydroxide or any other base [22]. In EF method, although in situ electrogeneration of reagents need complicated electrodes and conditions [23], we used iron electrodes (anode & cathode) due to the simplicity and possibility of industrialization of the method.

The objective of this paper is degradation and removal of sulfolane in a petrochemical wastewater using EF method because advantages such as cost, time, simplicity, efficiency and industrialization capabilities.

2. Experimental

2.1. Chemicals and materials

Sulfolane with purity of 99% as an organosulfur compound was obtained from Sigma-Aldrich (England). A solution of hydrogen peroxide (H_2O_2, 30%) was bought from Lamers & Pleuger (Netherlands). Sodium sulfate (Na_2SO_4), sodium chloride (NaCl), sodium hydroxide (NaOH), carbon tetrachloride (CCl_4) with purity > 99.8%, hydrochloric acid (HCl, 37%) and sulfuric acid (H_2SO_4, 95%–98%) were obtained from Merck (Darmstadt, Germany). Ferric chloride ($FeCl_3$) was purchased from Honeywell Riedel-de Haën (Seelze, Germany).

Working standard solutions were prepared daily by suitable dilution of the stock solution using pure water. Stock and working standard solutions were stored at 4°C in the refrigerator. Pure water was prepared by OES (Overseas Equipment & Services) water purification system (OK, USA). Wastewater samples were obtained from the treatment unit of an Iranian Petrochemical Company.

2.2. Experimental apparatus and procedure

Batch experiments were performed in a cylindrical electrolytic reactor (glass beaker) containing 1,000 mL solution (Fig. 1). Electrolyses were operated at constant current (I) using a DC power supply (Model 8303) from Iran Electronics Industries Co., (Iran). One pair of 5 cm × 10 cm cast-iron anode and cathode plates was positioned from each other and was dipped in the wastewater. A magnetic stirrer (Model IKA® C-MAG HS7, Germany) provided the mixing of the solution in the rector. In each run, wastewater sample was transferred to the electrolytic reactor. Then, a selected amount of sodium sulfate as supporting electrolyte was dissolved in the wastewater and conductivity of sample was checked using conductivity Meter (Model S30-K SevenEasy) from Mettler Toledo (Switzerland). The initial pH value was adjusted using concentrated sulfuric acid
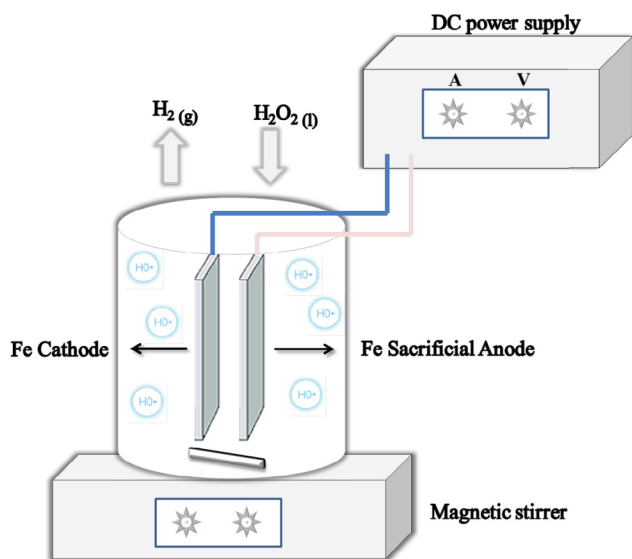
Fig. 1. The schematic diagram for electro-Fenton batch reactor that is a feasible technique for degradation of sulfolane with producing hydroxyl radicals.

or sodium hydroxide (0.1 M). The pH was measured by a digital pH meter (model 691) from Metrohm AG (Herisau, Switzerland). Hydrogen peroxide was added to the sample all at once. The EF experiment was started after the addition of the required amount of H_2O_2 and experiment was ended after a certain time and the process was quenched without adding sodium hydroxide or any other base. Then samples were settled for 30 min to sludge and solids were settled down.

The supernatant was passed through a paper filter, round S&S 598/1 (Filters by Schleicher & Schuell, Germany) and the filtered sample was analyzed in GC. It should be noted here, the preliminary experiments indicated that the paper filter did not adsorb any sulfolane. Samples were analyzed using a Chrompack CP 9000 GC equipped with Flame Ionization Detector (FID). The aqueous samples were directly injected to GC and chromatographic separation was made on a packed column (5% Carbowax 20 m, Chrompack, USA). High purity nitrogen was used as the carrier gas with a head pressure of 180 kPa. The temperature of the injection port was set to 230°C and the injection was set on splitless mode with 5.00 μL injection volume. The initial temperature was set to 190°C, which was isothermal and was held constant for 25 min. The FID detector temperature was set to 250°C. External calibration was used to quantify the sulfolane in the sample by preparing various concentrations of sulfolane as standards and the detection limit for sulfolane analysis using this method was 1 ppm. The relative standard deviation (RSD) for measuring 50 and 100 ppm (4 measurements) are within 5%. Chemical oxygen demand (COD) values of samples were determined by using closed reflux method described in the standard method [24]. Biochemical oxygen demand (BOD_5) measurements were performed via (BOD Trak II) manometric BOD analyzer from HACH co. (Colorado, United States).

The removal efficiency was calculated using Eq. (3).

$$R\% = \left[\frac{(y_o - y)}{y_o} \right] \times 100 \qquad (3)$$

where %R is the removal efficiency of sulfolane concentration/COD/BOD; and y_o and y are the initial and present quantities of measured parameters, respectively. All data reported were the average of three independent samples.

GC-SCD method was used for investigation of transformation products of sulfolane degradation. Samples were extracted using CCl_4 and analyzed using a Chrompack CP 9001 gas chromatograph (GC) equipped with a Sulfur Chemiluminescence Detector (SCD SIEVERS, model 355). Each 100 mL sample was extracted with 20 mL of CCl_4. After the extraction process, 1 mL of the CCl_4 layer at the bottom of the vials was transferred into a GC vial using a pasturing pipette. A fused silica capillary column (CP-SIL 5 CB for sulfur, Chrompack, USA) was used for the GC-SCD analysis with helium as the carrier gas with a head pressure of 300 kPa. The injection mode was splitless, with an injection volume of 1.0 μL and an injection temperature of 200°C. The temperature of burner as detector of device was 800°C. The oven temperature was programmed as follows: 90°C hold for 5 min; increase by 6°C/min to 200°C; maintain at 200°C for 15 min.

The extracted samples in CCl_4 were analyzed with GC-FID with other column and condition (A fused silica capillary column CP wax 52 CB from Chrompack, USA). High purity hydrogen was used as the carrier gas with a head pressure of 60 kPa. The injection mode was split with 10:1 split ratio, with an injection volume of 1.0 μL and an injection temperature of 230°C. The oven temperature was programmed as follows: 50°C hold for 5 min; increase by 8°C/min to 80°C; then increase by 2°C/min to 110°C; then increase by 20°C/min to 210°C maintain at 210°C for 20 min). The temperature of FID detector was 240°C.

Also extracted samples were analyzed with GC-MS Agilent (GC Agilent 7890A equipped with 5975C mass spectrometry detector, USA) with a fused silica capillary column (BP20 from SGE, Carolina, USA). The injection mode was splitless, with an injection volume of 1.0 μL and an injection temperature of 270°C. High purity helium was used as the carrier gas with a flow rate of 1 mL min⁻¹. The oven temperature was programmed as follows: 40°C hold for 4 min; increase by 1°C/min to 270°C; maintain at 270°C for 30 min. To trace the sulfur element during the degradation process, the total sulfur analyzer was used. Hence the extracted samples in CCl_4 were analyzed with elemental analyzer Multi EA®5000, Analytik Jena, Germany.

2.3. Characteristics of petrochemical wastewater

Wastewater samples for this work were taken from an Iranian Petrochemical Company that uses sulfolane in its process. The wastewater samples were spiked with the sulfolane at different concentration levels. During the study, characteristics of the wastewaters were re-determined before each EF runs, and the average values obtained from the experiments are given in Table 1. As seen, COD

Table 1
General characteristics of wastewater used in this study

Parameter	Average value
EC (μS cm^{-1})	342
pH	6.7
Sulfolane (mg L^{-1})	160
COD (mg L^{-1})	300
BOD$_5$ (mg L^{-1})	41
TSS (mg L^{-1})	30

and BOD$_5$ values of the wastewater are not too high. Approximately, these types of wastewaters can be categorized as weak wastewater. Also the conductivity of wastewaters is too low and for the electrochemical treatments are needed supporting electrolytes.

2.4. Experimental design

Design of experiments by using statistical methods such as response surface method (RSM) was utilized previously in many different processes [25–28]. Minitab® 19.0, PA, USA software was used for designing experiments as well as for regression analysis of the obtained experimental data. In this study, the central composite face-centered design and response surface methodology were used to design the experiments and evaluate the significance of individual factors and their interactive influences with minimum number of tests and obtain optimum operating conditions. The main effects of three independent factors: pH of the solution, dosage of hydrogen peroxide and current density were investigated using a central composite face-centered design (CCF). In the preliminary tests, three important parameters were studied independently. The data ranges of pH 2–6, H$_2$O$_2$ dosage 0.5%–3% (v/v) and current density 5–35 mA cm^{-2} were selected to understand how each factor affected the EF process. Afterwards, CCF was conducted to obtain the highest removals of sulfolane. A three factor, three levels CCF with 20 runs was employed. For the three-factor experiment of CCF, eight (2^3) factorial points, six axial points (2 × 3) and six center runs, a total of 20 experimental runs can be evaluated. The three factors were selected pH, H$_2$O$_2$ dosage and current density which were denoted as X_1, X_2 and X_3 respectively. Each factor was studied at three different levels, upper level correspond to +1, the basic level 0, and the lower level −1, these codifications are important in order to simplify the conditions for recording

experimental data and making results easier to utilize [29]. The experimental design applied in this work is shown in Table 2.

A full quadratic model with regression coefficients was chosen to fit the experimental data. Other than intercept, linear, and quadratic terms, this model additionally considers two-way interactions [Eq. (4)]:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{1 \leq i \leq j}^{k} \beta_{ij} X_i X_j \qquad (4)$$

where Y is the removal efficiency of sulfolane; β_0, β_i, β_{ii} and β_{ij} are the regression coefficients for intercept, linear, quadratic and interaction terms, respectively, and X_i and X_j are referred to the values of independent variables. According to 2^3 central composite face-centered design, a set of experiments were carried out. In Table 3, the experimental results after performing 20 runs are shown.

2.5. Statistical analysis

Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA) through statistical analysis software (Minitab® 19.0) for graphical analyses of the data to obtain the interaction between the process variables and the responses. The statistical significance was checked by the Fisher F-test, and model terms were evaluated by the p-value (probability) with 95% confidence level. The quality of the fit polynomial model was expressed by the coefficient of determination R^2 and adjusted R^2 in the same program.

3. Results and discussion

3.1. Preliminary experiments

Important parameters that influence the efficiency of contaminant removal by electro-Fenton process include: pH, hydrogen peroxide dosage and current density. Other parameters including temperature, electrode distance, type and amount of support electrolyte and time of treatment have less effect on removal efficiency. To examine the effect of the above-mentioned process parameters, some preliminary experiments was done. According to the experiments, the three most effective parameters, current density, hydrogen peroxide dosage and pH were selected for use in the experiment design. Fenton's reactions take place in the acidic range and removal efficiency was tested in this region but in very acidic pHs, due to the formation of H$_2$O$_3^+$ ion, the efficiency of hydroxyl radical formation

Table 2
Coded levels and independent variables for electro-Fenton process

Coded levels	X_1	X_2	X_3
	pH of the solution	Dosage of hydrogen peroxide (v/v %)	Current density (mA cm^{-2})
−1	2	0.5	5
0	4	1.75	20
1	6	3	35

Table 3
Design matrix for the 2^3 central composite face-centered design (CCF) validation conditions and responses

	X_1	X_2	X_3	% Removal	
Run	pH of the solution	Dosage of hydrogen peroxide (v/v %)	Current density (mA cm^{-2})	Experimental	Predicted
1	1	1	1	18.568	19.688
2	−1	1	1	93.936	89.339
3	0	0	0	15.969	16.560
4	0	1	0	30.696	35.658
5	0	0	0	16.836	16.560
6	0	0	0	15.103	16.560
7	0	0	0	14.237	16.560
8	−1	0	0	78.346	73.082
9	1	−1	1	18.568	14.491
10	0	0	−1	13.370	10.708
11	1	0	0	15.103	19.025
12	−1	1	−1	95.668	100.081
13	−1	−1	−1	48.888	48.103
14	0	0	0	17.702	16.560
15	0	−1	0	13.370	7.070
16	1	−1	−1	4.707	9.639
17	0	0	1	6.440	7.763
18	1	1	−1	28.097	22.201
19	0	0	0	16.836	16.560
20	−1	−1	1	38.493	44.724

decreases [30]. Also at high pH, hydrogen peroxide decomposes into water and oxygen and thus the removal effieincy is reduced [31]. Hence, the proposed range for pH in the acidic region of 2 to 6 was given to the software. According to preliminary experiments were performed and their results that high current density increases the temperature of the solution sharply and makes disturbance in treatment, the current density range of 5 to 35 mA cm^{-2} was given to the Minitab® software. The percentage of H$_2$O$_2$ was given to the software in the range of 0.5% to 3% by volume, according to the preliminary tests and their results that the removal of this contaminant was very small in amounts less than 0.5%. To investigate temperature on treatment, it was concluded that high temperatures have a negative effect on the removal of contaminants in EF. As well as during electro-Fenton process temperature of solution increase several degrees. Therefore, the ambient temperature was selected for this treatment. Regarding to selection of the type of supporting electrolyte, sodium chloride and sodium sulfate were investigated and sodium sulfate was selected as a supporting electrolyte based on pervious report [32]. The effect of electrode distances and time of treatment were investigated separately.

3.2. Effect of electrode distances

The variation of removal efficiency during the reaction period under different Fe electrode distance is presented in Fig. 2. At a constant electric current, increasing the electrode gap results in enlarged ohmic drops and higher energy consumption, which leads, in turn, to a significant temperature increase that can affect the interfacial properties of the multiphase medium, and alter treatment efficiency. As expected, sulfolane removal is a decreasing function of the electrode gap, as shown in Fig. 2. The optimal electrode distance is 10 mm for this equipment in consideration of the treatment cost and efficiency together.
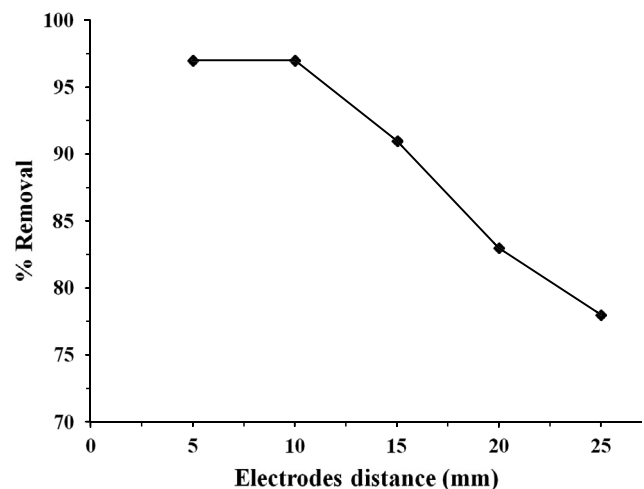

Fig. 2. Effect of distances between electrodes on sulfolane removal efficiency by electro-Fenton method: H$_2$O$_2$ = 0.98 mol L^{-1} (3% v/v), pH 2.5, current density = 15 mA cm^{-2}.

3.3. H_2O_2 addition

To investigate the single effect of hydrogen peroxide on oxidation of sulfolane without using electro-Fenton system, one liter samples of wastewater with 100 ppm of sulfolane were stirred for 1 h with the addition of different amounts of hydrogen peroxide. The obtained results is shown in Fig. 3. As seen, increasing the percentage of hydrogen peroxide has led to an increase in removal, but this removal rate is much less than using electro-Fenton.

3.4. Optimized conditons

The optimization involved the following steps: (i) performing the statistically designed experiments according to the design, factors, and levels selected; (ii) estimating the coefficients of the mathematical model to predict the response; and (iii) checking its suitability. The arrangements of CCF experiments are listed in Table 3, which include 20 sets of electro-Fenton experiments. By using multiple regression analysis, the sulfolane removal were correlated with the three design factors using the second-order polynomial [Eq. (4)]. The quadratic regression model for sulfolane removal (Y, %) in terms of coded factors are given by Eq. (5).

$$Y = 141.4 - 66.97X_1 + 18.40X_2 + 1.101X_3 + 7.373X_1^2 + 3.07X_2^2 - 0.0326X_3^2 - 3.942X_1X_2 + 0.0686X_1X_3 - 0.098X_2X_3 \quad (5)$$

Experimental values were the measured response data for a specific run, and the predicted values were assessed from the model and generated for the same run. As the predicted data were consistent with the observed values, the obtained second-order regression models were adequate for the prediction of response. The response model exhibited a good fit to the experimental data. Accordingly, the models were considered adequate for the predictions and refinement.
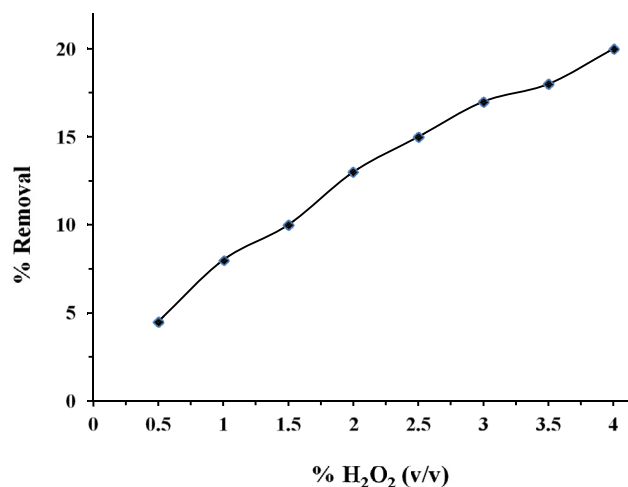

Fig. 3. Effect of addition of hydrogen peroxide alone on oxidation of sulfolane without using electro-Fenton system.

Statistical testing of the model was done with the Fisher's statistical test for analysis of variance (ANOVA). The results of the ANOVA for sulfolane removals are shown in Table 4. The ANOVA of these responses showed that the model is greatly significant as is evident from the value of $F_{statistic}$ (mean square due to regression/mean square to real error), (F_{model} = 56.17) and probability value that it is very low (P = 0.0001). Probability value (P-value) lower than 0.01 indicated that the model is considered to be statistically significant. The response surface plots to estimate the removal efficiency over independent variables shown in Fig. 4. These graphical representations are derived from the models of Eq. (5).

Experimental data of sulfolane removal were statistically treated and Fig. 5 presents the standard Pareto chart,

Table 4
Analysis of variance (ANOVA) for the RSM model of sulfolane removal

| Source	DF	Adj. SS	Adj. MS	F-Value	P-Value
Model	9	14,283.9	1,587.10	56.17	0.000
Linear	3	9,370.2	3,123.40	110.54	0.000
X_1	1	7,305.4	7,305.37	258.55	0.000
X_2	1	2,043.2	2,043.15	72.31	0.000
X_3	1	21.7	21.69	0.77	0.402
Square	3	4,075.8	1,358.62	48.08	0.000
X_1^2	1	2,392.1	2,392.12	84.66	0.000
X_2^2	1	63.5	63.47	2.25	0.165
X_3^2	1	147.5	147.52	5.22	0.045
2-Way interaction	3	837.8	279.27	9.88	0.002
$X_1 \times X_2$	1	776.8	776.83	27.49	0.000
$X_1 \times X_3$	1	33.9	33.86	1.20	0.299
$X_2 \times X_3$	1	27.1	27.11	0.96	0.350
Error	10	282.6	28.26		
Lack-of-fit	5	274.4	54.89	33.75	0.001
Pure error	5	8.1	1.63		
Total	19	14,566.4			
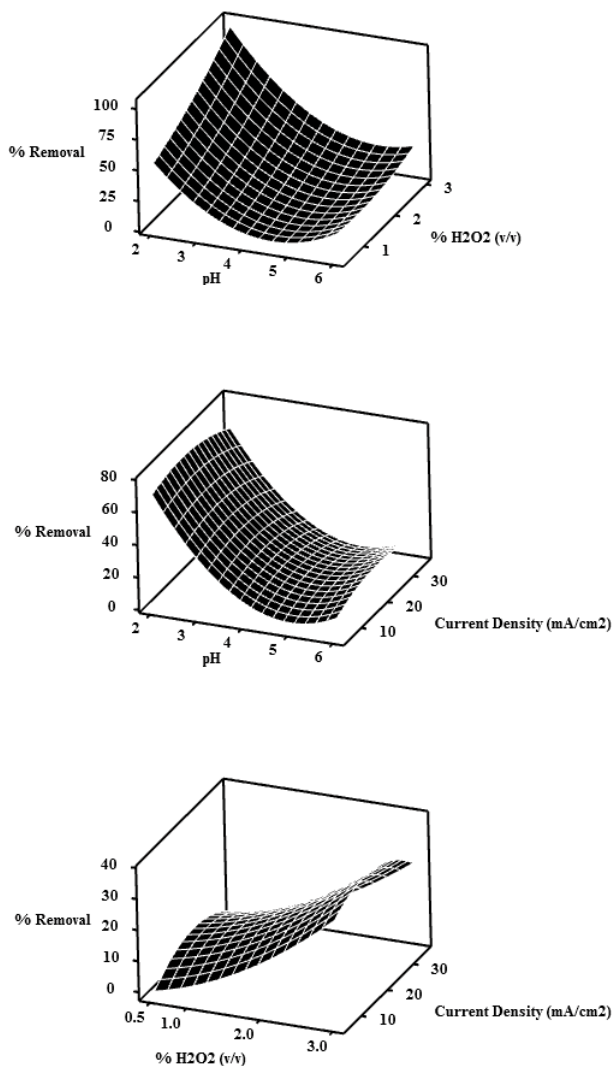
Fig. 4. The response surface plots to estimate the removal efficiency over independent variables.

which shows the effects of the variables on the efficiency of removal of sulfolane. The pH has the most impact on efficiency and current density did not affect this response to a statistically significant level. Based on the overlay plot, the optimum conditions for current density, pH and H_2O_2 dosage are, respectively, 15 mA cm^{-2}, 2% and 3% (v/v). These values were also experimentally approved. Due to the formation of $H_2O_3^+$ ion, the efficiency of hydroxyl radical formation decreases in high acidic conditions (pH lower than 2.5) [30]. Therefore, pH 2.5 was selected for optimal conditions and the initial pH of the watewater was adjusted to 2.5 by added sulphuric acid since it was expected to increase during the treatment. It should be noted that during the electro-Fenton process, the acidification of the solution is reduced due to the formation of metal hydroxyl, and the strength of the Fenton reactions is also reduced. Finally, this increase in pH continues to maximize contaminant removal and quench Fenton reactions. At the end of the 1-h process, the measured pH of the solution was neutral and equivalent to 6.8.
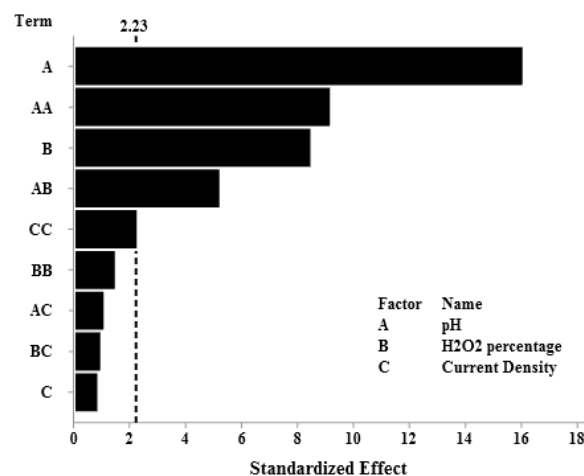

Fig. 5. Standard Pareto chart, which shows the effects of the variables on the efficiency of removal of sulfolane.

3.5. Degradation pathway of sulfolane

One of the concerns about $^\bullet$OH based treatment is the potential formation of toxic intermediates such as low-molecular weight aldehydes [7]. Therefore, chromatographic techniques were used to approximate the path of the degradation process and to identify the intermediates and products of degradation.

Two samples (100 mL) of wastewater befor and after treatment were extracted using 20 mL of CCl_4. After the extraction process, 1 mL of the CCl_4 layer at the bottom of the vials was transferred into a GC vial for later usage. These two extracted samples injected to GC-FID with a fused silica capillary column (CP wax 52 CB from Chrompack). The GC-FID chromatograms are presented in Fig. 6. Obviously, the peak of sulfolane is seen at retention time of 37.8 min. Decreasing of height of peak after treatment shows the removal and degradation of sulfolane. For investigation of intermediates and products of degradation process, it was necessary to analyze the samples before and after treatment using the GC-MS and identify the details of their compounds. The extracted samples were injected to GC-MS and their results were compared and investigated carefully (Fig. 7). In the pre-treatment sample, sulfolane peak was detected at retention time of 47.15 min. As seen in Fig. 7b, the peak of sulfolane and some peaks related to other organic substances were removed, but no new compounds were created during treatment. Sulfolane and some fractions of hydrocarbons were removed with the high efficiency, showing the effectiveness of electro-Fenton treatment in sulfolane removal. Therefore with GC-MS it was proved that degradation of sulfolane by EF method goes on completely oxidation and converting to carbon dioxide and water. Also CO_2 is released by hydrogen bubbles.

Complete degradation of target organic contaminants in water as the advantage of electro-Fenton method was reported previously [33]. Also, in order to investigate the transformation of sulfolane to other sulfur-containing compounds, the samples (before and after treatment) were injected into the GC-SCD. According to the obtained
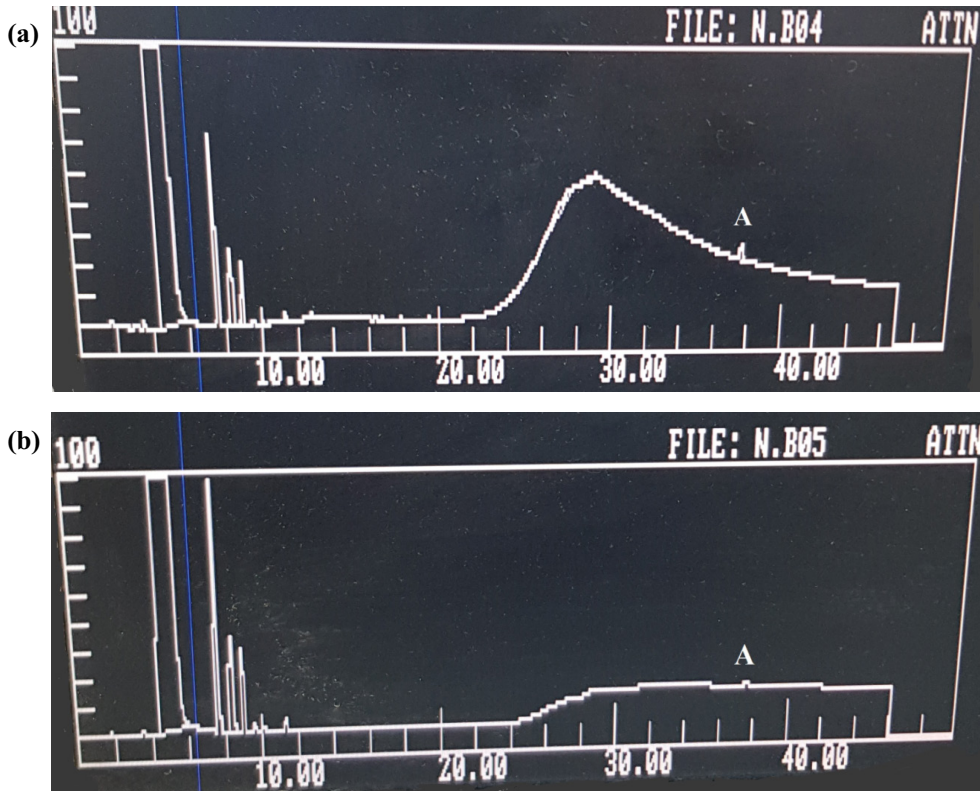
Fig. 6. Chromatograms of GC-FID analyses of (a) raw wastewater and (b) electro-Fenton treated wastewater samples. A: sulfolane with the retention time of 37.8 min.
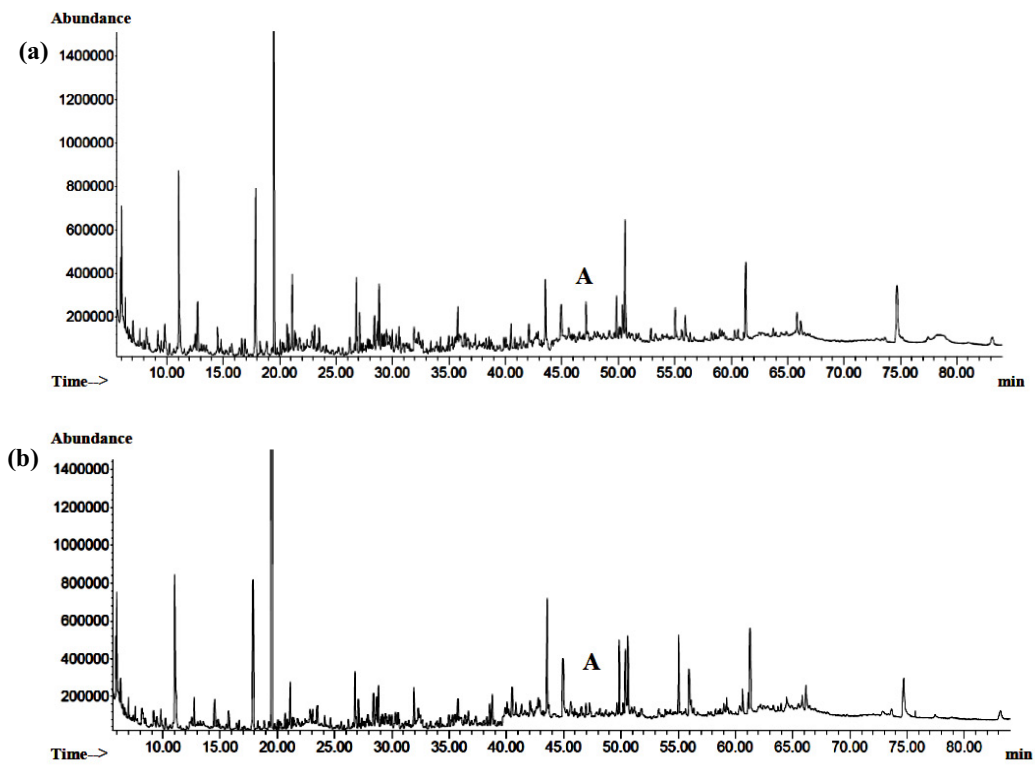

Fig. 7. Chromatograms of GC-MS analyses of (a) raw wastewater and (b) electro-Fenton treated wastewater samples. A: sulfolane with the retention time of 47.15 min.

chromatograms, the only sulfur-containing compound in the sample befor treatment was sulfolane which was removed from the sample after treatment. Using the total sulfur analyzer to prove the removal of sulfolane as a organosulfur compound from the sample after treatment and the amount of elemental sulfur was measured by total sulfur analyzer device and compared with the sample before treatment. Reducing the amount of sulfur from 50 ppm to trace amount (<1 ppm) indicates approximately complete elimination of the pollutant and elemental sulfur was released as SO_2 from wastewater. Due to the complete degradation of sulfolane and oxidation to carbon dioxide the proposed degradation pathways is shown in Fig. 8.

3.6. Comparison methods

To evaluate and confirm the electro-Fenton method, the results of the proposed method were also compared with the electrolysis and Fenton methods. In Fig. 9, the removal percentage of sulfolane (100 ppm) vs. time is shown for electrolysis, Fenton's reagent and electro-Fenton method. The Fenton's reagent was used in acidic condition, H_2O_2 = 0.98 mol L^{-1}, $FeCl_3$ = 0.065 mol L^{-1} and pH 3 [8]. Two iron electrodes with a distance of 1 cm, neutral pH 6.8 and current density 15 mA cm^{-2} were used in electrolysis method.

As shown in Fig. 9, electrolysis method is not able to remove contaminants without the presence of Fenton reagents and the electro-Fenton method was able to significantly remove a higher percentage of sulfolane in less time (30 min for electro-Fenton method in comparison to 120 min. for Fenton reagent).

3.7. Characteristics of wastewater after treatment

After treatment of a sample under optimal conditions, the other characteristics of the sample were invenstigated (Table 5). In addition to the high percentage of sulfolane removal, the removal percentage for other parameters such as COD and BOD_5 were obtained 55 ± 5 and 43 ± 5, respectivly.

3.8. Initial concentration effect

Samples containing different amounts of sulfolane were treated under optimal conditions at time 1 h. The removal percentage of different concentrations was calculated and its graph was plotted (Fig. 10). According to the results, increasing the initial concentration of sulfolane leads to
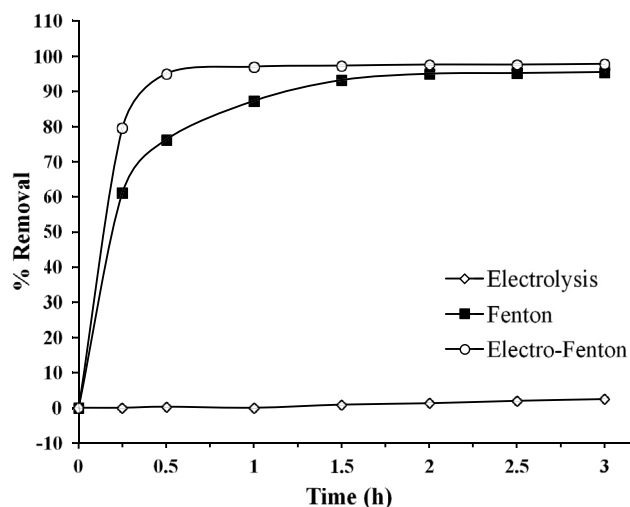

Fig. 9. Comparison of sulfolane removal by electrolysis, Fenton's reagent and electro-Fenton method. Electrolysis: pH 6.8, current density = 15 mA cm^{-2}, d = 1 cm; Fenton's reagent: H_2O_2 = 0.98 mol L^{-1} (3% v/v), $FeCl_3$ = 0.065 mol L^{-1}, pH 3; electro-Fenton method: H_2O_2 = 0.98 mol L^{-1} (3% v/v), pH 2.5, current density = 15 mA cm^{-2}, d = 1 cm.

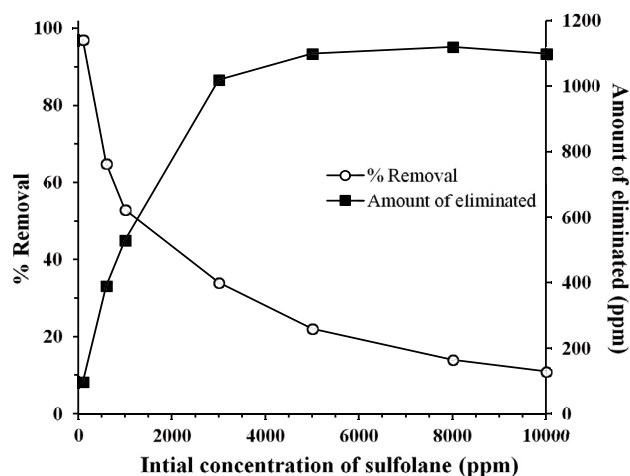
Fig. 10. The effect of initial concentration of sulfolane on removal efficiency at optimal conditions: H_2O_2 = 3% v/v, pH 2.5, current density = 15 mA cm^{-2}, d = 1 cm.
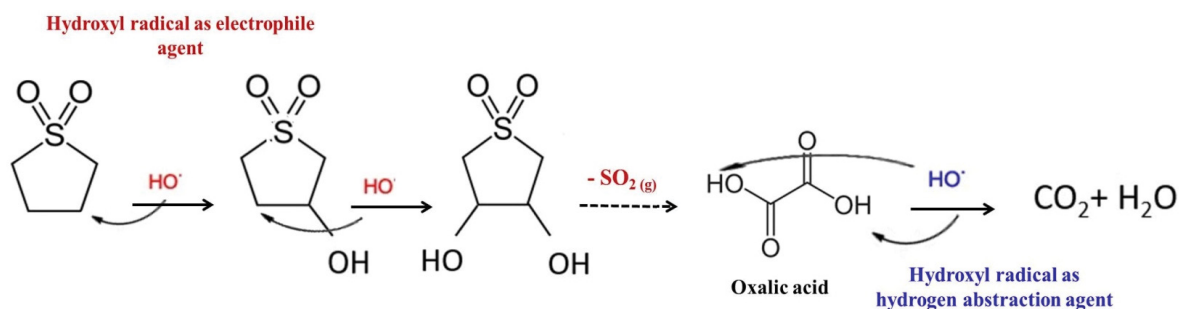

Fig. 8. Proposed pathways for degradation of sulfolane by electro-Fenton method.

a decrease the removal percentage and this system can degrade the limited amount of sulfolane. The concentration about 1,000 ppm sulfolane as the its limited amount in wastewater can eliminate by this system in 1 h.

3.9. Volume of sludge produced

High sulfolane removal efficiencies can not be the only criteria for selecting an electrochemical technique for wastewater treatment. The fraction of water recovered after treatment is also an important decision criterion in selecting this technology. In comparison with the volume of treated water, the amount of sludge produced has to be low enough for possible use of electro-Fenton at the industrial-scale. Sludge volume for wastewater was measured after electrolytic treatment and settling of solid matter that was treated in various times by electro-Fenton. The results shown in Fig. 11 were obtained without adding the flocculating agent, after natural settling of the waste treated for 24 h in a 50 cm high cylinder with a diameter of 10 cm. According to results, after 1 h treatment the volume of sludge becomes significant and this is undesirable for water recovery after treatment.

3.10. Energy and iron consumption and effect of supporting electrolyte

The iron electrode consumption is calculated from Faraday's law from the following equation [34,35]:

$$W = \frac{I \cdot t \cdot MW}{Z \cdot F} \tag{6}$$

where W is the iron dissolved (g); I is the current (A); t is the contact time (s); MW is the molecular weight (g mol^{-1}); Z is the number of electrons involved in the redox reaction (equals 2 for iron); and F is the Faraday's constant (96,500 C/mol of electrons). Fig. 12 shows the estimated amount of iron dissolved as a function of time for a current density 15 mA cm^{-2}. The figure shows that the rate of electrode erosion at this current density is about 26.1 mg min^{-1}. This is a theoretical value and this amount was measured in practice and averaged for several treatments. In 1 h, the amount 1.2 g iron per L or kg m^{-3} of wastewater (with the practical rate of electrode erosion 22 mg min^{-1}) was consumed, practically. Also, based on current density and treatment time, the amount of energy consumption is 16.5 kWh m^{-3}.

By adding a supporting electrolyte at the beginning of treatment, the energy consumption decrease. The effect of addition of different amounts of sodium sulfate as supporting electrolyte on energy consumption (kWh m^{-3}) is shown in Fig. 13. Due to low electrical conductivity of this type of wastewater we proposed adding at least 1 g L^{-1} supporting electrolyte to reduce energy consumption.

Although the aerobic biodegradation and adsorption methods are two popular methods for treating sulfolane pollutant from water and wastewater, they are often not fast enough and have a lower removal rate than advanced
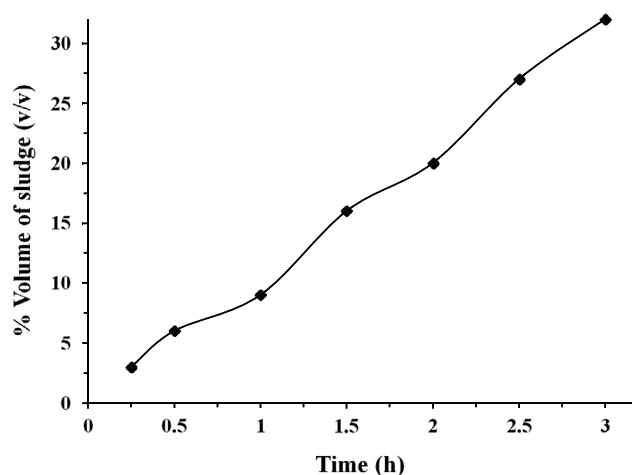
Fig. 11. Volume of sludge produced at various time under optimal conditions of removal: H$_2$O$_2$ = 3% v/v, pH 2.5, current density = 15 mA cm^{-2}, d = 1 cm.

Table 5
Characteristics of wastewater after 1 h treatment under optimum conditions

BOD$_5$ (mg L^{-1})	23	43
COD (mg L^{-1})	135	55
EC (µS cm^{-1})	11,200	–
Parameter	Average value after EF	% Removal
pH	6.8	–
Sulfolane (mg L^{-1})	4	97.5
TSS (mg L^{-1})	18	40

Table 6
Comparison of the present method with some other advanced oxidation processes for degradation of sulfolane

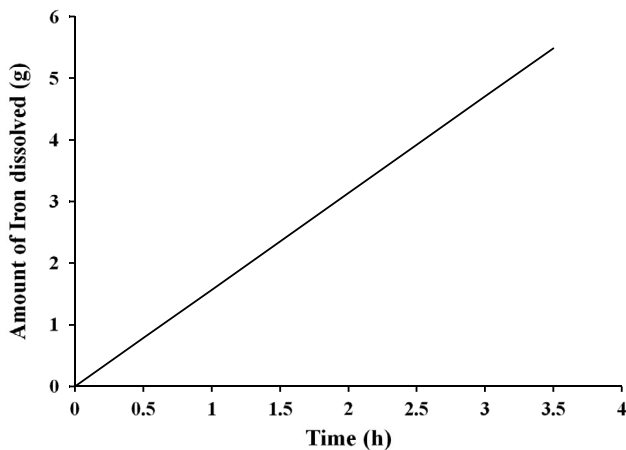| Treatment method	% Removal	Time (min)	Reference
Electro-Fenton	97.5	60	This study
Fenton's reagent	95	180	[8]
Pressurized ozone/H$_2$O$_2$	99	350	[9]
UV/O$_3$/H$_2$O$_2$	99	60	[10]
UV/O$_3$	80	60	[11]
CaO/O$_3$	100	150	[12]
CaO$_2$/O$_3$	100	40	[12]

Fig. 12. The estimated amount of iron dissolved as a function of time for a current of 1.5 Å (current density of 15 mA cm^{-2}).
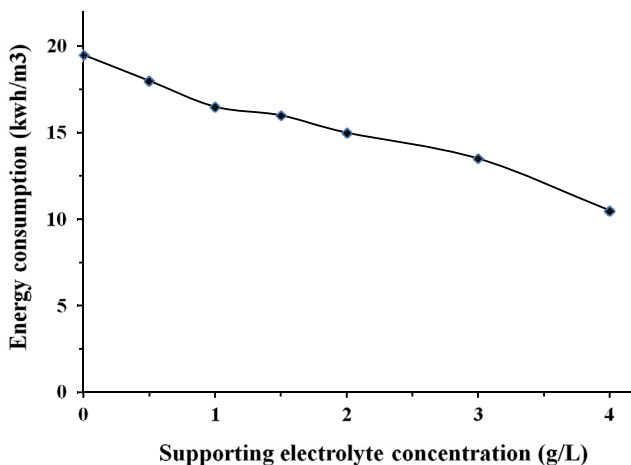

Fig. 13. The effect of addition of different amounts of sodium sulfate as supporting electrolyte on energy consumption (kWh m^{-3}).

oxidation processes. Also, due to the high polarity and mobility of sulfolane, physical removal methods did not have high removal efficiency [7]. Recent studies have focused on advanced oxidation methods in the degradation of this contaminant, which are compared in Table 6 with the proposed method. In the present method, with a simple design with the capability of industrialization and without the use of UV light or ozone gas, which has the problems of cost, supply and storage of ozone gas, we achieved high efficiency in a short time.

4. Conclusion

The main goal of this study was using electro-Fenton as an advanced oxidation process for treatment of sulfolane. The effect of major parameters on E-Fenton process was evaluated using response surface methodology with face centered-central composite design. The treatment efficiency was found to be function of the initial pH, applied current density and H_2O_2 dosage. It was proved

that sulfolane could be fast and successfully removed by E-Fenton method. The removal percentage of sulfolane in 1 h was 97.5% and in half an hour was 95%. As the sulfolane was removed, other wastewater parameters such as COD and BOD were reduced under optimal conditions. The removal percentages of COD and BOD were 55% and 43%, respectively. The degradation pathway and the transformation products were investigated using GC-FID, GC-MS, GC-SCD and total sulfur analyzer. It was proved that sulfolane completely was degraded and it was oxidized to carbon dioxide and water. No sulfur-containing compounds were formed as degradation products and elemental sulfur was released as SO_2. Transformation products were investigated and no new substance except CO_2 and H_2O or new contaminant was formed during the degradation of sulfolane.

Acknowledgments

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