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Abstract

Iraqi gas oil with sulfur content 9400 ppm was desulfurized electrochemically at constant current (300 mA), the process consists two steps; first step is electrochemical desulfurization by using electrochemical cell contains two graphite electrodes while the used electrolyte is NaCl to enhance electrolyte electrical conductivity, and hydrogen peroxide as an oxidant agent, second step is extraction with acetonitrile. Optimization of process parameters was done by applying response surface methodology RSM combined with Box –Behnken experimental method, in which the sulfur removal efficiency was acted as response function while the reaction temperature, NaCl concentration and time were selected as controllable (studied) variables. The sulfur removal efficiency was ranged from 55.84 % to 88.07%. The results were analyzed with Design-Expert software by fitting with second order polynomial model and the empirical model was exhibited high correlation factor (R^2=0.9966) and the estimated optimization solution stated that maximum sulfur removal efficiency is 88.611% at temperature (57.656 ℃), NaCl concentration (0.106 M) and, time (51.46 min.).

Keywords:
Oxidative desulfurization, Design experiment, Box- Behnken, ANOVA.

1. Introduction

Organic sulfur compounds contained in fuel still a main source for air pollution because of sulfur oxides emissions SO_x when the fuel combustion, on the other hand presence sulfur in petroleum products may cause corrosion of refineries equipment (pipes, columns, heat exchangers etc.) and cause poisoning of high valuable catalyst at upstream refineries units[1], for those bad consequences sulfur removing from petroleum products must be done . There are many techniques used to remove sulfur but the conventional method is hydrodesulfurization process HDS; HDS technique is needed harsh operation condition e.g. elevated temperature and hydrogen partial pressure and it was need to provide suitable catalyst [2]. Some other techniques were suggested as alternative technologies for sulfur removal from fuel such as extraction, oxidation, alkylation, adsorption, BioDesulfurization, membrane separation and their

combinations [1].

Oxidation desulfurization usually consists two steps; first step is sulfur organic compounds oxidation it was during this step a chemical substances as oxidant such as hydrogen peroxide , proxy acid and ionic liquid [3] whereas sulfur compounds are converted to sulfoxide and sulfone as in Fig. 1,while the second step is solvent extraction [1],or distillation[4]. A new technology of oxidation technology for oxidation desulfurization was suggest by many researchers , this technique is electrochemical oxidation which work with low oxidant consumption as well as small wastewater amounts [5]. Electrochemical – extraction technique was used for sulfur content reduction from many petroleum products. The aqueous NaCl solution used to enhance electrolyte electrical conductivity while the cell was composed from two graphite electrodes[3].
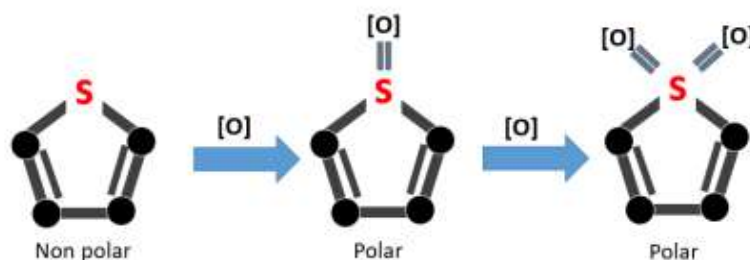

Figure 1: Oxidization desulfurization process of sulfur organic compounds (i.e. thiophene).

Fig. 2 illustrate proposed mechanism for oxidation is that may be came from high active oxidative radical; hydroxyl active radical with hypochlorite anion were abstained via electrochemical oxidation for water and chloride anion [1] as well as via formation water oxide H_2OO from hydrogen peroxide as first step and transfer oxygen from water oxide as a second step to the nucleophile [6]. Thus desulfurization by oxidation with hydrogen peroxide was suggested that hydroxyl radicals to form sulfoxide (contains S=O) and these are further converted to sulfones (contains O=S=O) [7].

The oxidation step was followed by extraction step in which extraction organic sulfides was markedly depended on polarity and solubility. As mentioned above sulfoxide and sulfones were abstained by oxidation step, and as know these polar compounds while sulfides are non-polar compounds and they are easily extracted by a polar solvent [1].

Phase transfer catalyst PTC is an agent was added in a small amount which lead to enhance the reaction rate between compounds founded in different phases (immiscible liquids), in other word it's the agent has ability to transfer materials from one phase to another phase so the reaction will be possible [8].
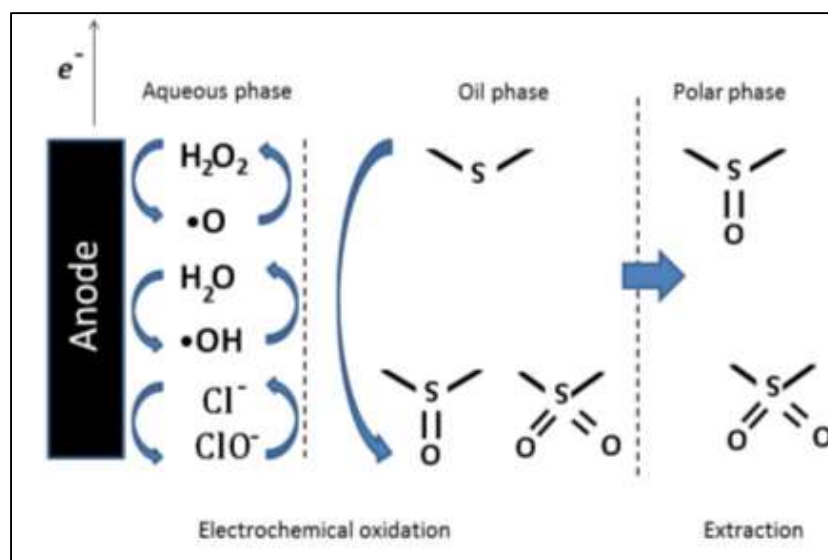
Figure 2: Mechanism of formation high active oxidative medium and sulfur removing by electrochemical and extraction.

The present study it was gas oil desulfurization by oxidation –extraction technique, in which the oxidation done by electrochemical process. The experiments were designed by using Box-Behnken experimental design, in which this method is most frequently used from response surface methodology RSM methods; it is offered some advantages when compared with other RSM methods; few numbers of experiment required to cover the design ranges with high efficiency [2]. A Box – Behnken design was used here to study the effect of electrolysis temperature, NaCl concentration and electrolysis time on sulfur removal efficiency, optimization sulfur removing efficiency and explaining the mathematical relationship between response and studied variables (empirical model).

2. Experimental

2.1 Feedstock and chemicals

Iraqi gas oil (sulfur content 9400 ppm) provided from Najaf refinery used as feedstock, Analytical grade chemicals and reagents used in this study hydroxide peroxide H_2O_2, sodium chloride NaCl, glacial acetic acid CH_3COOH, Acetonitrile CH_3CN. All the regents and solvents used in this study obtained from Sigma-Aldrich with their standard purity.
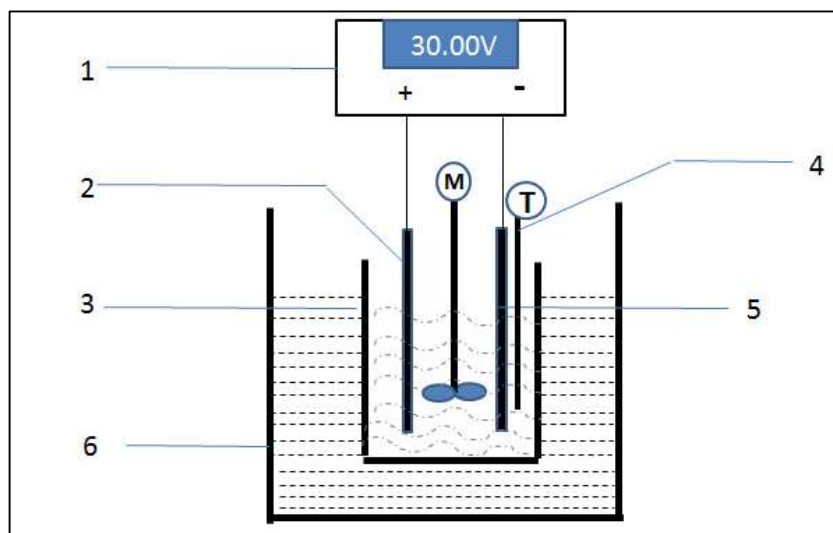
2.2 Experiment method

Electrochemical desulfurization done at two steps in which the electrochemical cell apparatus in Fig. 3; first step is oxidation, the electrochemical oxidative experiments were carried out in electrolysis cell have two electrodes made from graphite at distance 2 cm, while electrolyte is contains NaCl solution as supporting electrolyte to enhance electrical conductivity for electrolyte , 10 ml of hydrogen peroxide as oxidant agent and 5 ml of 10% acetic acid solution as

phase transfer catalyst . 95 ml of gas oil was added to the cell, adjust temperature and power on power supply at 300 mA and 30 V, after specific time the power was switch off. The gas oil and electrolyte are layered Second step is solvent extraction for removing oxidation products by adding 5 ml of acetonitrile to 10 ml of desulfurized gas oil. The total sulfur content was measured before and after electrochemical-extraction desulfurization by using Sulfur meter model RX-620SA/TANKA SCINTIFIC. And the sulfur removal efficiency calculated by using equation (1):

$$S\% = \frac{S_0 - S_f}{S_0} \times 100 \qquad\qquad .... \qquad (1)$$

Where S% is sulfur removing efficiency, S_0 is initial sulfur content, S_f is final sulfur content.

Figure 3: Electrochemical desulfurization experimental sketch (1-power supply, 2-anode, 3-electochemical cell, 4-thermostatic sensor, 5-cathode, 6-water bath).

2.3 Response surface methodology RSM

The conventional methods for experimentation were studied effect of controllable variables by varying one variable and holding others at certain value, and this step will be repeated with other variables (varying one and hold other constant), this technique help to determine the relationship for response magnitude with studied variables but it was failed to predict the interaction effect between variables .This technique is time consuming [9]. Applying the RSM leads to understand the process better and reduced the number of runs required to cover the range of studied variables , these runs important for generation statistically validation results with optimization the process .The application Box-Behnken design here was used to optimized the process by determine mathematical relationship between response (sulfur removal efficiency Y) and studied variables (temperature X_1, NaCl concentration X_2 and time X_3.) the result were

analyzed by aim of Design expert software version 11 (Stat- Ease, In. Silicon Valley, CA, USA). Table 1 shows the studied (independent) variable with their levels.

Table-1: Studied variables range and levels.

Variable	symbols	levels		
		-1	0	1
Temperature (℃)	X_1	40	50	60
NaCl Concentration (M)	X_2	0.1	0.2	0.3
Time (minutes)	X_3	30	45	60

The total number of runs required for covering the three selected variables with their levels is calculated by below equation (2) [10]:

$$N = 2k(k-1) + r \quad\quad \dots\dots\dots \quad\quad (2)$$

Where *N* is number of experiments, *k* is number of variables, and *r* is replicate number of central points (3 -6) [10]. The statistical analysis for actual experiment results were fitted as second order polynomial as shown in equation (3):

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j + e \quad \dots\dots\dots\dots (3)$$

Where Y is response (sulfur removal efficiency); X_i and X_j are studied variables; b_0, bi, bii and bij are intercept, linear, square and interaction coefficients respectively and *e* is model error.

3. Result and discussion

3.1 Empirical model

The actual experimental results were shown in Table 2, the sulfur removal efficiency ranged from 55.84 to 88.07, while Table 3, listed summary of analysis of variance ANOVA, the correlation coefficient R^2 is 0. 9966.The results were analyzed by aim of Design-Expert software to get the empirical model for sulfur removal efficiency as a function of independent variables (temperature, NaCl concentration and time) which as below:

$$Y = 80.75 + 8.45\,X_1 - 4.77X_2 + 2.63X_3 - 0.82X_1X_2 + 3.72X_1X_3 + 1.14X_2X_3 - 6.62X_1^2$$
$$- 0.1017\,X_2^2 - 8.75X_3^2 \quad \dots\dots\dots\dots \quad (4)$$

Table-2: Experimental design and actual value for removal efficiency Y (response).

run	variables			sulfur removal efficacy Y
	Temperature (℃) X_1	NaCl Concentration(M) X_2	Time (minutes) X_3	
1	50	0.1	60	78.16
2	50	0.2	45	79.17
3	60	0.3	45	76.89
4	60	0.1	45	88.07
5	50	0.2	45	82.12
6	40	0.3	45	61.63
7	60	0.2	30	67.48
8	40	0.1	45	69.53
9	50	0.2	45	80.97
10	50	0.3	30	63.36
11	60	0.2	60	80.18
12	50	0.1	30	75.18
13	40	0.2	30	58.02
14	50	0.3	60	70.9
15	40	0.2	60	55.84
	R²	0.9966		
	Adjusted R²	0.9904		
	Predicted R²	0.9923		

The F – value as shown in Table 3 is 162.05 which greater than tabulated value in Fisher F-test standard distribution table ($F_{9, 5,0.05} = 4.77$) , and that refer as good indication for suggested second order polynomial and is highly significance . The effects of independent variables on response are ordered according its significant as follows; temperature, NaCl concentration and time due to their F-value 571.22, 182.22 and 55.34 respectively in table 3. Examination of p-value help to study the significance of all terms in empirical model; the terms X_1, X_2, X_2^2 and X_3^2 are high significant because of small p-value (less than 0.0001). Comparison between actual experimental results with predicated result for sulfur removal efficiency was shown in Fig.4 with a 45º line, as seen all points were diverged very small from regression line via high R^2 (0.9966).

Table-3: results of ANOVA for Y (response)

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	1289.75	9	143.31	162.05	< 0.0001
Temperature (ºC) X_1	571.22	1	571.22	645.93	<0.0001
NaCl Concentration (M) X_2	182.02	1	182.02	205.02	<0.0001
Time (minutes) X_3	55.34	1	55.34	62.57	0.0005
X_1X_2	2.69	1	2.69	3.04	0.1416
X_1X_3	55.35	1	55.35	62.59	0.0005
X_2X_3	5.2	1	5.2	5.88	0.0598
X_1^2	161.89	1	161.89	183.07	< 0.0001
X_2^2	0.0382	1	0.0382	0.0432	0.8436

|					
$X_3{}^2$		282.8	1	282.8	319.79	< 0.0001
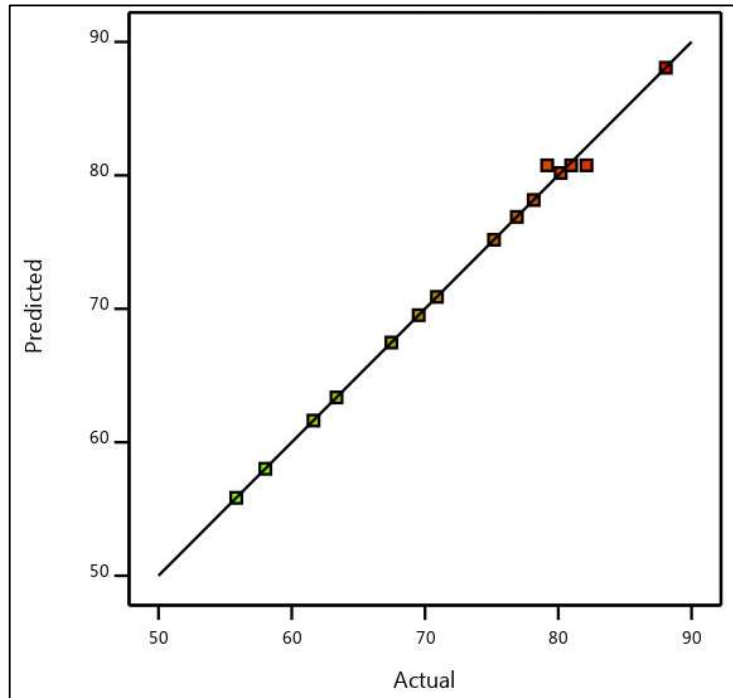
Figure 4: Comparison between the actual and predicated response values for PNT removal efficiency.

3.2 Effect of studied variables

Effect of each studied variables on sulfur removal efficiency was shown in Fig.5, as seen in figure sulfur removing efficiency was increased with temperature of electrolysis and reached to temperature 55ºC and decreasing with further temperature increasing, it was complicated to explain this behavior because temperature accelerate rate of oxidation reaction [11]. On the other hand, the additional increasing in temperature may had disadvantages due to non-conductivity for reaction because heat releasing from electrochemical oxidation as well as water electrolysis which lead to evolution of oxygen that cause energy losses [12]. NaCl concentration exhibit opposite effect on removing efficiency because limitation of side reaction and solubility of chlorine via increasing chlorine evolution, the evaluated gases molecules were accumulated with time and this may cause sulfur removing efficiency decreasing as shown in Fig. 5.
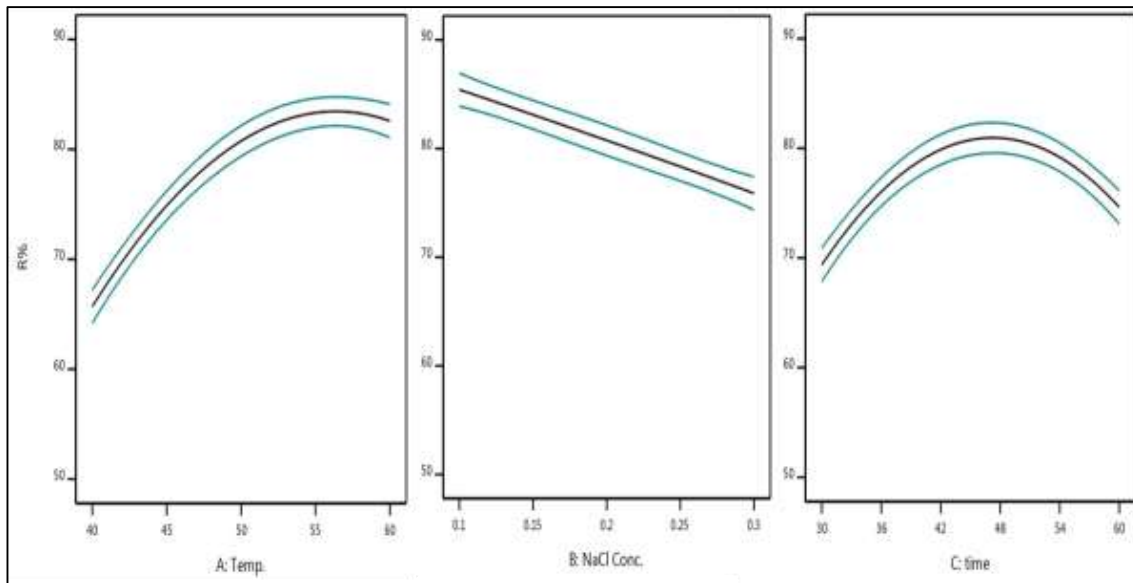
**Figure 5:** Effect of individual variables on sulfur removal efficiency

3.3 Interaction effect of studied variables

The interaction effect of studied variables on sulfur removing efficiency can be shown by plotting contour chart which predicated by aim of Design Expert software, according to empirical model as in equation (4).

Fig.6 illustrated interaction effect of temperature and NaCl concentration on sulfur removing efficiency which increased from 65% to 85% at any concentration of NaCl within temperature range 40 -60 ℃, while the interaction of temperature and time was shown in Fig.7; the maximum sulfur removing efficiency predicated about 83.4 % as illustrated within small surface in contour chart which indicated that sulfur removing efficiency is high sensitive for interaction of both variables (temperature and time). Fig.8 shows the contour plot for effect of both NaCl concentration and time on sulfur removing efficiency, as shown the removal efficiency increased from 65% to 85% when NaCl concentration increased from about 0.11 M to 0.27M at any time.
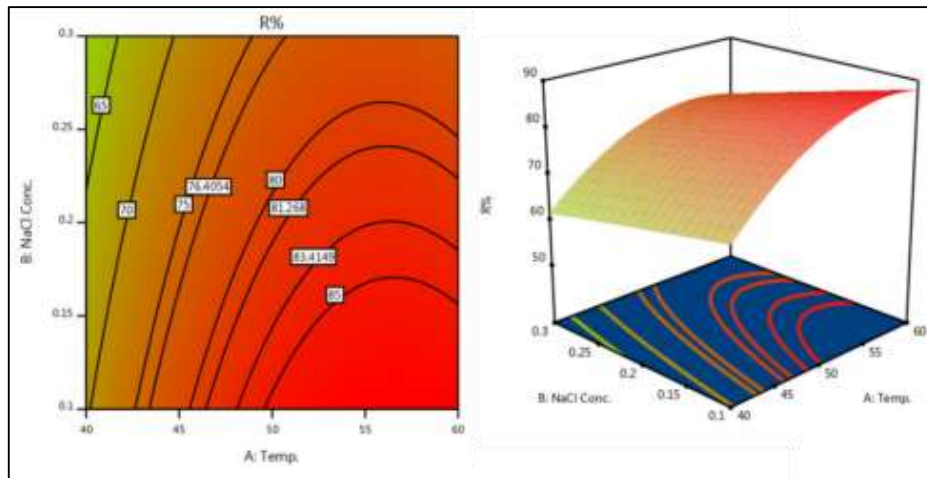
Figure 6: combined effect of temperature and NaCl concentration on sulfur removal.
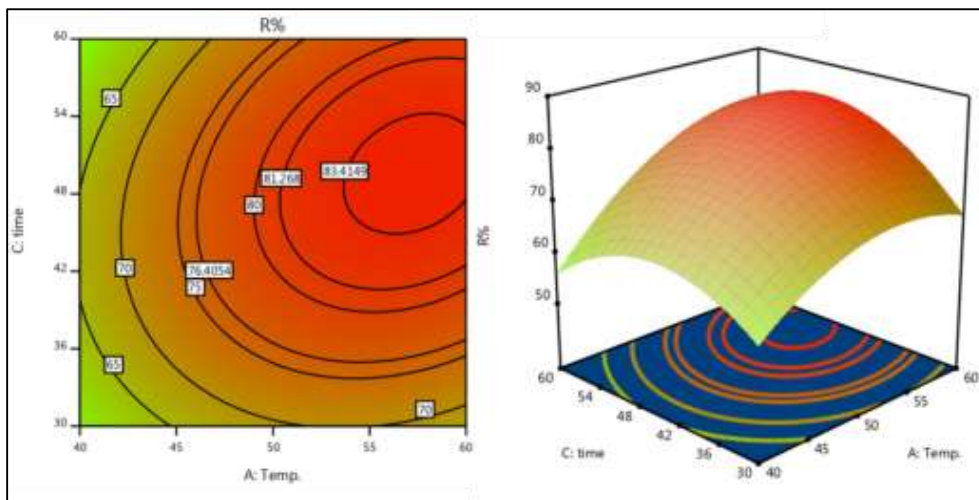
Figure 7: Combined effect of temperature and time on sulfur removal.
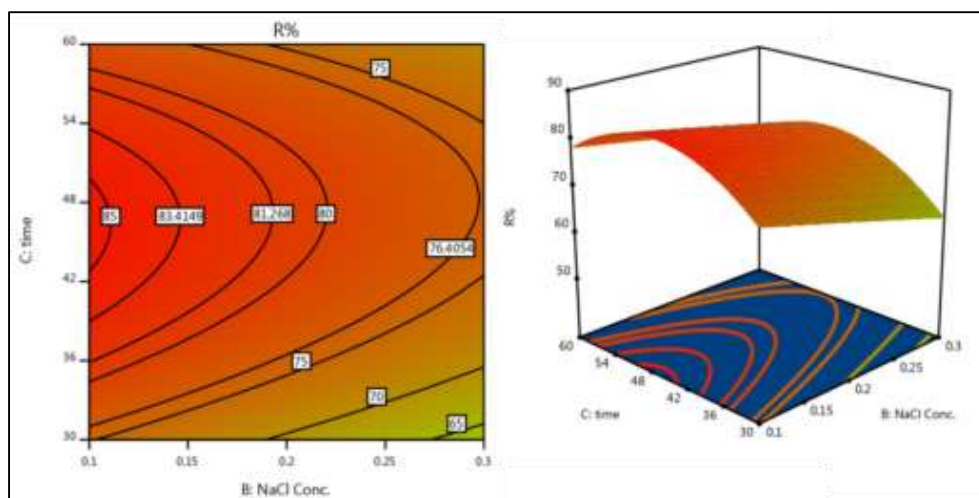
Figure 8: Combined effect of time and NaCl concentration on sulfur removal.

3.4 Optimization

Numerical optimization is one of important function was provided by Design Expert software, so the lower and upper limits for all studied variables with its response as indicated by empirical model were used to find the maximum response which satisfy desired requirements. Constraints of studied variables and response were shown in Table 4, while Table 5 shows the solution that fulfilled all specified conditions for response (sulfur removal efficiency), thus according to Design Expert software optimum conditions solutions were found are 100 solutions . Table 4: constraints each variables for numerical optimization of response.

Type of variable	Goal	Lower limit	Upper limit
A:Temperture (ºC)	is in range	40	60
B:NaCl concentration(M)	is in range	0.1	0.3
C:Time (minutes)	is in range	5.73866	8.26134
Sulfur removal efficiency (%)	maximize	55.84	88.07

Table 5: Optimum conditions for maximum PNT removal efficiency

No.	Temperature (ºC)	NaCl Conc.(M)	Time (min.)	PNT removal efficiency (%)	Desirability
1	57.656	0.106	51.465	88.611	1.000

4. Conclusion

This study showed that electrochemical oxidation – extraction successes for removing sulfur from gas oil. The empirical model estimated by application of RSM and Box-Behnken experimental method was show good fitting via high R^2 (0.9966) .Optimization for this system were established by using serious of experiments runs were designed according to Box – Behnken DOE. ANOVA analysis shows that significance of studied variables on sulfur removal efficiency at order; temperature, NaCl concentration and time due to their F-value 571.22, 182.22 and 55.34 respectively. The optimum conditions were lead to maximum removal efficiency are temperature (57.656 ºC), NaCl concentration (0.106 M) and, time (88.611 min.)

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