Desulfurization of Basra Diesel Fuel by Emulsification – Adsorption Processes

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Abstract

In this study, the combined emulsification–adsorption processes were employed for the desulfurization of Basra diesel fuel. A high sulfur diesel fuel of 1.4538 wt% from the Basra refinery was oxidized effectively with H2O2 and Acetic acid (AcOH) as a catalyst to reduce sulfur content to 1.0875 wt% before being emulsified. The emulsification desulfurization (EDS) process using Alkyl benzene sulfonate (ABS) as a surfactant was optimized by 20 trails according to Response Surface Methodology (RSM). A 0.83886 wt% was achieved at the following optimum conditions: Surfactant concentration 20 wt.%, temperature 57.56 ^{o}C, and homogenization speed 5695 rpm. The adsorptive desulfurization (ADS) process using activated bentonite clay was carried out in a batch system. The RSM was applied to determine the effect of contact time (1-10 hr), clay mass (5- 20 gm/50ml), and temperature (30-100 ^{o}C) on the sulfur removal. Results showed that the sulfur content of 0.57 wt% was achieved at the following conditions: adsorption time 7.18 hrs., temperature 53.3 ^{o}C, and clay mass 15.24 gm/ 50ml. The achieved sulfur removal efficiency was 23% and 32% for EDS and ADS respectively. The diesel fuel quality was studied by GC and IREX.

Keywords: Diesel fuel, Desulfurization, RSM, Emulsification, Adsorption.

إزالة الكبريت من وقود ديزل البصرة عن طريق الاستحلاب – عمليات الامتزاز

الخلاصة:

في هذه الدراسة، تم دمج عمليتي الاستحلاب والامتزاز لازالة الكبريت من وقود الديزل لمصفى البصرة. تم تقييم مواصفات الديزل المحسن المستخرج من هاتين العمليتين والبديلة لعملية الهدرجة باستخدام العامل المحفز حيث تم تحسين خصائص الديزل باستخدام تقنية التصميم التجريبي (طريقة احصائية)RSM. تم إجراء 20 تجربة مختبرية في كل عملية. تمت أكسدة وقود الديزل عالي الكبريت بنسبة 1.4538% نسبة وزنية من مصفى البصرة بشكل فعال باستخدام H2O2 وحمض الأسيتيك (AcOH) كعامل محفز لتقليل محتوى الكبريت إلى 1.0875% نسبة وزنية قبل دخوله الى عملية استحلاب. تم ادخال وقود ديزل مصفى

البصرة المؤكسد ذو المحتوى الكبريتي 1.0875% وزنا الى عملية الاستحلاب. تم دراسة تأثير إزالة الكبريت بواسطة الاستحلاب على وقود الديزل المؤكسد باستخدام خافض الشد السطحي ألكيل بنزين سلفونيت. تم تحقيق نسبة كبريت للديزل 0.83886% وزنا في الظروف المثلى التالية: تركيز الكيل بنزين سلفونيت 20% وزنا، درجة الحرارة 57.56 درجة مئوية ، وسرعة الخلط المتجانس 5695 دورة في الدقيقة. تم ادخال الديزل الناتج من عملية الاستحلاب الى عملية الامتزاز باستخدام طين البنتونايت المنشط في نظام الدفعات. تم تطبيق تقنية التصميم التجريبي (RSM) لتحديد تأثير زمن التلامس (10-1 ساعة) وكتلة الطين (5- 20 جم / 50 مل) ودرجة الحرارة (100-30 درجة مئوية) على إزالة الكبريت. أظهرت النتائج أن محتوى الكبريت 0.57% وزنا قد تحقق في الظروف التالية: زمن الامتزاز 7.18 ساعة ودرجة الحرارة 53.3 درجة مئوية وكتلة الطين 15.24 غم / 50 مل. تمت دراسة جودة وقود الديزل بواسطة تحاليل GC وIREX .

1. <u>Introduction</u>

Growing global energy consumption, stringent environmental legislation on transportation fuels, and decreasing oil sources have all combined to produce a triangle of limits that have posed significant problems to refiners in recent years. Economic and demographic growth are predicted to drive up energy demand. Crude oil demand, a cheap source of energy that now accounts for 34.5% (v/v) of the global energy mix, is predicted to expand at a 0.8% annual rate through 2023 [1]. Petroleum is made up of a variety of hydrocarbons as well as sulfur, nitrogen, and oxygen molecules. Heavy crude oil contains sulfur in the form of sulfides, disulfides, mercaptans, thiophenes (T), benzothiophenes (BT), dibenzothiopenes (DBT), benzonaphthothiophenes (BNT), and dinaphthothiophenes (DNT) [2].

Sulfur in liquid fuels is highly undesirable, and many products' sulfur concentration is rigorously regulated [3]. Sulfur lowers the quality of the oil used to make final products, and hence the commercial value of the liquid fuel. Jet fuel, diesel, and gasoline are the main categories of transportation fuels, and each has a unique composition and set of characteristics. Due to the sulfur content in these transportation fuels, which is currently the cause of environmental pollution, diesel fuel contains the most refractory sulfur compounds, including BT, DBT, and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) [4].

Fuel oils with sulfur components, such as gasoline and diesel fuel, result in higher CO and particle emissions, decreased combustion efficiency, catalyst deactivation, and SO_X emissions during combustion [5]. Acid rain, ozone layer degradation, and decreased soil fertility are all consequences of SOx air pollution [6]. These factors led environmental protection organizations all over the world to adopt strict regulations on the sulfur content in liquid fuels [7][8] . Since 2018, the countries spanning around 50% of the earth's area have been compelled to use on-road diesel with extremely little sulfur (10- 15 ppm), especially for transportation utilities [9]. The

removal of sulfur-containing compounds from fuel oil has been accomplished using several approaches, including hydrodesulfurization (HDS), bio-desulfurization (BDS), adsorption, and oxidative desulfurization (ODS) [8] [10]. To remove sulfur from petroleum fractions, petroleum refineries currently use HDS as a common method [11] [6]. Using hydrogen gas, the hydrodesulfurization reaction occurs in the presence of catalysts (Ni, Co, and Mo) at high temperatures (up to 400 °C) and pressures (up to 100 atm) [12]. It is a well-known method for getting rid of sulfur-containing organic molecules that are aliphatic and acyclic [13].

The steric hindrance that results from adsorption on the catalyst surface prevents HDS from being as successful at removing heterocyclic S compounds like (T), (BT), and (DBT) and their derivatives as it is at removing aliphatic S compounds like thiols, thioethers, and disulfides [14] [15][5]. Additionally, HDS encourages a detrimental effect on the octane rating of treated fuel and encourages the unintended hydrogenation of aromatic compounds without sulfur [16].

With its mild reaction conditions and effective desulfurization capability, ODS functions the best among all novel desulfurization technologies[17] [18] [19]. The oxidation reactivity appears to rise, DBT > 4,6-DMDBT > BT > T in the reverse reactivity sequence of HDS. ODS is produced in two stages: (1) oxidation of aromatic sulfur-containing compounds in distillates, and (2) removal of sulfoxides or sulfones (oxidized sulfur-containing compounds) via extraction or adsorption [20]. Because refractory heterocyclic sulfur compounds such as T, DBT, and their derivatives are easily removed by ODS, it is currently being investigated as a possible way to achieve an ultra-low S-level in fuel oil due to its ease of processing and high efficiency [14].

Hydrogen peroxide (H_2O_2) has been demonstrated to be the most effective oxidant among various oxidant due to its low cost, eco-friendliness, wide availability, and high concentration of active oxygen [21] [22]. H_2O_2 is the most common oxidizing agent because it is the most environmentally friendly. Typically, H_2O_2 is used in the presence of a catalyst such as acetic acid, or formic acid [23] [24]. However, the use of H_2O_2 for ODS applications requires an extra separation method afterward the oxidation reactions, declining the overall reliability and efficiency of the technology [16]. To enhance the ODS efficiencies, the technology was investigated by integration with other similar technologies such as emulsification-adsorption.

The ODS process involves the oxidation of divalent sulfur to its corresponding hexavalent sulfur of sulfones. This electrophilic addition reaction of oxygen atoms to the hexavalent sulfur of

sulphones results in the removal of a substantial portion of the existing sulfur, making the remaining sulfur compounds amenable to efficient removal. The chemical and physical properties of sulfones are significantly different from those of hydrocarbon molecules [25].

The main problem is related to the presence of two reaction phases: an oil phase with the sulfur compound and a polar phase that contains the oxidant (H_2O_2), which is not soluble in the oil phase [26]. For this reason, some authors have studied the use of phase transfer catalysts [27]. Then, the sulfones obtained are transferred to the polar phase due the solubility of sulfones in a polar solution, giving the production of a sulfur free polar phase [27][28]. But still, mass transfer limitations make this reaction too slow for industrial use so some very interesting approaches have been studied, including the use of microemulsions. Emulsions can be also produced using surfactants as they play a significant role in the reduction of surface or interfacial tension [29].

In this research, ABS anionic surfactant was used for reduction the interfacial tension between two phases. The emulsification promotes the mass transfer of oxidized sulfur compounds to water phase by increasing the surface area between two phases (Oil and water) which consequently enhances the extraction rate. The emulsification process results in a significant gain in the interfacial area, which allows for the rapid transfer of solutes between the two phases [30].

Some potential benefits of adsorption for desulfurization are the mild operating temperature and the low sulfur levels that could be achieved if refractory sulfur compounds are removed. In the adsorption process, the sulfur compound is selectively adsorbed by the adsorbents without any reaction [31]. A high-sulfur diesel fuel containing 1.4538 wt% of total sulfur content underwent a series of processes to reduce its sulfur content. The first step involved an oxidative desulfurization (ODS), which resulted in a reduction of sulfur content to 1.0875 wt%. An emulsification by ABS surfactant process was then employed, which utilized to further reduce the sulfur content to 0.8388 wt%. Finally, the diesel fuel was subjected to adsorption by bentonite clay, which further reduced the sulfur content to 0.57 wt%.

The present work describes the structure models based on the statistical and mathematical methods of RSM to simulate the desulfurization efficiency by emulsification (EDS) (Surfactant concentration, Temperature, and Homogenization speed) and adsorption (ADS) (Contact time, Clay mass, and Temperature) conditions. Furthermore, the desulfurization efficiency of sulfur

compounds during the treatment processes was confirmed based on the results of gas chromatography GC analysis.

2. Material and Methods

Non-hydro-treated Basra diesel fuel with a total sulfur concentration of 1.4538 wt% provided by the distillation tower of the South Refineries Company (SRC)-Basra was employed as a feedstock. The properties of the diesel fuel are listed in Table (1).

Table (1) Properties of Basra diesel feedstock.

Property	Method	Value
Density@ 15.6 °C, g/cm3	ASTM D-1298	0.8215
API Gravity @ 15.6 °C	____	38.4
Kinematic viscosity @40 °C, cSt	ASTM D-445	3.48
Sulfur content(wt.%)	ASTM D-4294	1.4538
Cetane No.	ASTM D976	46
Diesel Index	IREX-test	43.3
Aromatics(vol.%)	IREX-test	27.1
PNA (vol.%)	IREX-test	4.3
Color (visual)	ASTM D-1500	1
Ash (%mass)	ASTM D-524	< 0.0010
Water and sediment(%vol.)	ASTM D-2709	0.025
Flash point	ASTM D-93	68
Distillation points: °C	ASTM D-86	
IBP		185.9
T10		229
T90		329.6
EBP		355.7

H_2O_2 was supplied by BDH Middle East, while AcOH and HNO_3 acid were supplied by SIGMA-ALDRICH. An anionic ABS surfactant was provided by the Vegetable Oils Company in Iraq, while bentonite clay was provided by the Iraqi National Company for Geological Survey and Mining in Baghdad.

2.2 EDS procedure

Diesel feedstock with a sulfur content of 1.4538 wt% was oxidized by peracid acid, which was generated by combining H_2O_2 and acetic acid as a catalyst in a 2:1 ratio. In 500 mL, the oxidation

agent was mixed with diesel fuel to lower the sulfur concentration to 1.0875 wt%. This was accomplished under the following conditions: oxidant ratio of 19.8 wt.%, temperature of 64.6 $^{\circ}$C, and reaction time of 89.3 minutes.

The previously oxidized diesel fuel was charged with an adequate amount of surfactant (ABS) for the emulsification process. The RSM statistical technique was used to optimize the effect of the parameters on the emulsification process (surfactant concentration wt.%, temperature $^{\circ}$C, and homogenization speed rpm) based on 20 experiments, as shown in Table (2).

A homogenizer was used to charge the amounts of (X_1=oxidized diesel wt%, X_2=ABS wt%, and 5 wt% deionized water) to a 500 ml standard conical flask-produced emulsion. Centrifuge the mixture for 5 minutes at 800 rpm before separating it into two components. With a syringe, the top oil phase was extracted for sulfur analysis.

2.2 ADS procedure

In 20 runs, acid-treated bentonite was employed for adsorption after the emulsification procedure as shown in Table 2. For activation of bentonite clay, it was ground to less than 75 μm particle size and washed out several times followed by drying at 110 $^{\circ}$C for 5 hr before being treated with HNO_3 acid. 10 gm of dry bentonite sample was mixed with 100 ml of 0.1 N HNO_3 for 1 hr. The clay slurry was then washed several times with deionized water until reached pH = 4. The sample was then dried in the oven at 110 $^{\circ}$C for 8 hr and mesh. Mixing 50 ml of diesel fuel with modified bentonite at different masses was charged to a 150 mL standard Pyrex beaker. The sample was mixed by stirring device for the different times, temperatures, and clay masses at 1200 rpm. Centrifuge the diesel fuel for 5 minutes at 800 rpm to separate the remaining clay from treated diesel and the diesel was reserved for sulfur analysis. The sulfur concentration was determined by the Energy Dispersive X-ray Fluorescence Spectrophotometer (EDXRF) technique HORIBA sulfur analyzer (SLFA-2100, Japan).

Table (2) The experiments trial in emulsification and adsorption desulfurization by RSM statistical technique.

	Emulsification Desulfurization			Adsorption Desulfurization		
	Surfactant	Temperature	Homogenization Speed	Time (hr.)	Temperature (ºC)	Clay mass (gm)
Run	(wt.%)	(ºC)	(rpm)			
1	10.5	70	10500	3.7	9.5	0.791
2	5.2	35	5222.2	1	12.5	0.763
3	5.2	60	15777.8	5.5	12.5	0.822
4	10.5	47.5	20000	5.5	12.5	0.615
5	10.5	47.5	10500	5.5	12.5	0.677
6	10.5	25	10500	5.5	12.5	0.678
7	15.7	60	5222.2	3.7	15.5	0.716
8	10.5	47.5	10500	10	12.5	0.618
9	10.5	47.5	10500	5.5	12.5	0.679
10	10.5	47.5	10500	3.7	9.5	0.713
11	15.7	35	5222.2	5.5	12.5	0.674
12	10.5	47.5	1000	3.7	15.5	0.621
13	15.7	60	15777.8	7.3	15.5	0.683
14	15.7	35	15777.8	5.5	5	0.762
15	5.2	35	15777.8	5.5	12.5	0.675
16	1	47.5	10500	7.3	15.5	0.566
17	10.5	47.5	10500	5.5	12.5	0.678
18	5.2	60	5222.2	7.3	9.5	0.623
19	20	47.5	10500	7.3	9.5	0.712
20	10.5	47.5	10500	5.5	20	0.588

Sulfur compounds are detected by using Trace sulfur analyzer (Sulfur Gas Analyzer – Model 4629, USA) uses sulfur chemiluminescence detector (SCD) according to the (ASTM D-5504 & ASTM D-5623). Concentrations of all relevant fuel components in diesel fuel before/after desulfurization are accomplished by using a spectral fuel analyzer (era spec, Austria) based on the standards (ASTM D-5845, D-6277, D-7777, D-7806, EN-238, EN-14078, ISO-15212, and IP559).

3. Results

Response Surface Method "RSM" is one of the most efficient approaches for designing and estimating second-order polynomials and it was employed in this work since it allows for the construction of a second order model without the necessity for a complete three-level factorial experiment. The emulsion fuel is prepared utilizing the high energy method, which involves using a high rotor-stator speed homogenizer to prepare the emulsion fuel. Surfactant concentration

(wt.%), temperature (ᵒC), and homogenization speed (rpm) were the process-effective parameters that had a substantial influence on emulsion preparation [32]. The resulted diesel fuel from the emulsification treated by adsorption process. A series of experiments were designed to examine the effects of process factors and their combined interactions on the adsorptive desulfurization process. They were conducted by adjusting process parameters such as temperature, time, and adsorbent loadings. The produced fuel under optimum condition of both EDS and ADS were examined by GC and IREX analysis to evaluate quality and the sulfur compounds of the treated fuel. Table 3 lists the outcomes of the desulfurization tests for both procedures. The Predicted and Experimental results of EDS and ADS desulfurization processes were illustrated in Figure (1).

For each treatment step, the (Co) represents the diesel fuel's starting sulfur level. To estimate the percentage of sulfur removal efficiency (RE%), each experiment was assessed separately to determine the sulfur concentration after treatment (Ce). From Eq. (1), the RE% in the emulsification and adsorption processes was estimated.

$$RE\% = (Co - Ce \, / \, Co) * 100 \qquad (1)$$

Table (3) The results of desulfurization experiments in EDS and ADS.

	Emulsification Desulfurization			Adsorption Desulfurization		
	Predicted Sulfur cont.	Experimental Sulfur cont.	Removal Efficiency	Predicted Sulfur cont.	Experimental Sulfur cont.	Removal Efficiency
Run	(wt.%)	(wt.%)	(RE.%)	(wt.%)	(wt.%)	(RE.%)
1	0.931	0.928	14.664	0.791	0.782	6.77
2	1.024	1.034	4.873	0.763	0.784	6.5
3	1.021	1.018	6.350	0.822	0.812	3.2
4	0.965	0.958	11.834	0.615	0.619	26.2
5	0.926	0.911	16.246	0.677	0.665	20.72
6	0.952	0.945	13.057	0.678	0.671	20.01
7	0.861	0.863	20.631	0.716	0.712	15.12
8	0.926	0.916	15.755	0.618	0.598	28.7
9	0.927	0.918	15.58	0.679	0.642	23.5
10	0.920	0.915	15.85	0.713	0.682	18.7
11	0.904	0.895	17.7	0.674	0.668	20.4
12	0.958	0.943	13.3	0.621	0.623	25.7

13	0.889	0.875	19.5	0.683	0.702	16.3
14	0.887	0.876	19.5	0.762	0.764	8.92
15	1.012	1.019	6.24	0.675	0.671	20
16	1.076	1.065	2.026	0.566	0.571	32
17	0.927	0.915	15.85	0.678	0.667	20.5
18	0.993	0.986	9.31	0.623	0.619	26.2
19	0.837	0.838	23	0.712	0.718	14.4
20	0.926	0.915	15.9	0.588	0.573	31.7

The feed for Emulsification process contains the 1.0875 wt %

First experiment condition resulted sulfur reduction to 0.928 wt%.

RE% = (1.0875 – 0.928 / 1.0875) * 100

RE% = 14.664

The feed for Adsorption process contains the 0.83886 wt %

First experiment condition resulted sulfur reduction to 0.782 wt%.

RE% = (0.8388 – 0.782 / 0.8388) * 100

RE% = 6.77
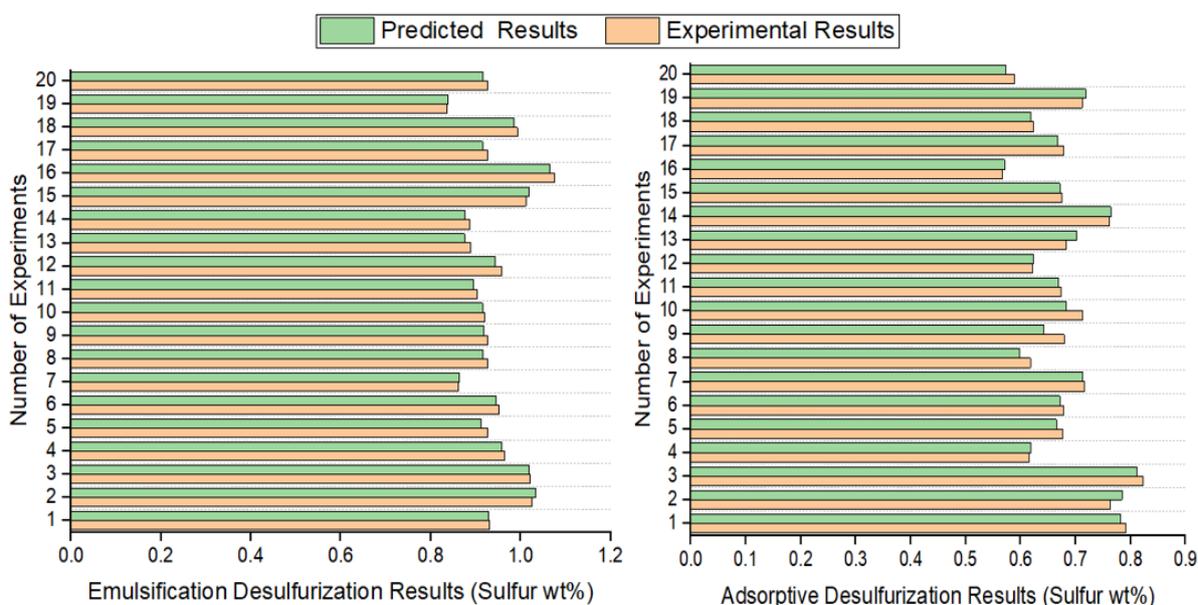
Fig. (1): Predicted and Experimental results of Emulsification and Adsorptive desulfurization processes.

4. <u>Discussion</u>

4.1 Analysis of variance

4.1.1   Emulsification process

Regression analysis was used to forecast the desulfurization rate during the EDS. ANOVA is essential to validate the relevance and fitness of the model; it indicates whether the developed quadratic model is relevant [33]. It looked into the impact of process factors and their interaction. Table (4) summarizes the results of the ANOVA analysis.

Table (4) Analysis of emulsification parameters by ANOVA.

Source	Sum of Squares	DF	square Mean	F value	Prob>F p-value	
Model	0.069	9	0.0077	184.49	< 0.0001	significant
A-Surfactant %	0.058	1	0.058	1400.22	< 0.0001	significant
B-Temperature ^oC	0.006	1	0.0006	14.43	0.0035	significant
C-Homogenization speed (rpm)	0.00028	1	0.00028	6.75	0.0265	significant
AB	0.000019	1	0.00002	0.47	0.5071	Not significant
AC	0.000069	1	0.00007	1.67	0.2249	Not significant
BC	0.00075	1	0.00075	18.15	0.0017	significant
A^2	0.00348	1	0.0035	83.41	< 0.0001	significant
B^2	0.00105	1	0.001	25.15	0.0005	significant
C^2	0.0023	1	0.0023	55.92	< 0.0001	significant

*Note that R^2= 0.9813, Adjusted R^2= 0.9798

One of the statistical metrics used to determine if F is large enough to indicate statistical significance is the P-value test. P-values less than 0.05 were deemed significant, whereas P-values more than 0.1 were deemed inconsequential. The ANOVA model's F-value (184.49) suggests that it is statistically significant. Furthermore, the P-test result (< 0.0001) demonstrates the significance of the regression model [34]. The parameters A, B, C, BC, A^2, $B^{2,}$ and C^2 are significant model terms. The Adj. R^2 of 0.9813 is reasonably consistent with the models' R^2 of 0.9798. The difference between anticipated and actual values is less than 0.2, indicating that they are quite near.

As shown in Table (3), the experiment 19 result EDS for the lowest percent sulfur content was obtained at 47.5 ^oC, 20% surfactant concentration, and 10500 rpm homogenization speed. As stated in Eq. 2, empirical models based on linear analysis were developed to expected responses for the desulfurization rate. The linear equation represents the effects of surfactant concentration

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in weight percent, temperature in degrees Celsius, and homogenization speed in revolutions per minute (rpm), as well as their combinations:

*%Sulfur content (Emulsification) = [(+0.91) - (0.067 * A) - (0.0065 * B) + (0.0046 * C) + (0.0016 * AB) - (0.0033 * AC) + (0.01 * BC) + (0.014 * A^2) + (0.008 * B^2) + (0.012 * C^2)]*   (2)

The negative coefficient values indicated that as the relevant variables of these coefficients grew within the tested range, desulfurization efficiency improved, whereas the positive coefficient values suggested the opposite impact. As demonstrated in equation 2, both parameters (A represents surfactant weight percentage and B represents temperature in degrees Celsius) contribute positively to sulfur content decrease, however, homogenization speed (C) has a negative influence. Surfactant concentration had the biggest influence, followed by reaction temperature and homogenization speed. The interaction and quadratic terms of the process parameters, on the other hand, contribute to the sulfur content having a limited influence.

4.1.2   Adsorption process

Table (5) shows the ANOVA analysis for sulfur component removal by an adsorption approach. The ANOVA model's F-value is 29.92, indicating that it is statistically significant. Furthermore, the P-value (0.0001) demonstrates the importance of the regression model. The variables (A, B, and C) have a substantial influence on the response; however, the interaction of the parameters had no significant effect. The Adjusted R^2 of 0.932 is in reasonable agreement with the models' R^2 of 0.9642.

Table (5) Analysis of adsorption parameters by ANOVA.

Source	Sum of Squares	DF	square Mean	F value	Prob>F p-value	
Model	0.088	9	0.0098	29.92	< 0.0001	significant
A-Time	0.018	1	0.018	54.77	< 0.0001	significant
B-Temperature	0.037	1	0.037	114.37	<0.0001	significant
C-Clay mass	0.016	1	0.016	47.86	< 0.0001	significant
AB	0.000105	1	0.000105	0.32	0.5825	Not significant
AC	0.00065	1	0.00065	2.01	0.1867	Not significant
BC	0.00027	1	0.00027	0.83	0.3847	Not significant
A^2	0.0014	1	0.00144	4.43	0.0617	Not significant
B^2	0.0038	1	0.0038	11.62	0.0067	significant
C^2	0.000116	1	0.000116	0.36	0.5645	Not significant

*Note that R^2= 0.9642, Adjusted R^2= 0.932.

After emulsification, the feed used in the adsorption desulfurization study had 0.8388 wt% sulfur. As demonstrated in Table (3), a minimal sulfur content was obtained in experiment 16 after 7.3 hours, 51 °C temperature, and 15.5 gm bentonite. An empirical link between the input variables (Time (A), temperature (B), and adsorbed dosage (C)) and sulfur content was produced (Eq.3) by utilizing the quadratic model to determine the relevance of parameters and the model efficiency of the polynomial model:

%Sulfur content (Adsorption) = [(+0.65) - (0.029 *A) + (0.045 * B) - (0.032 * C) + (0.00306 * AB) + (0.00922 * AC) + (0.00612 * BC) + (0.0049 * A^2) + (0.0080 * B^2) + (0.0014 * C^2)] (3)

The adsorption period and adsorbent dosage have a negative impact on the sulfur content; however, temperature has a favorable impact. The cross-product coefficients (AB, AC, and BC) have no effect on the desulfurization rate, however, B^2 has a considerable effect.

4.1.3 Parameters Effects and Optimum Results

The optimal results indicated that the emulsification process was used to achieve the sulfur content of 0.83886 weight percent at the following conditions: surfactant concentration 20 weight percent, temperature 57.56 °C, and homogenization speed 5695 rpm. Figure (2) depicts the process desirability and the ideal outcomes.
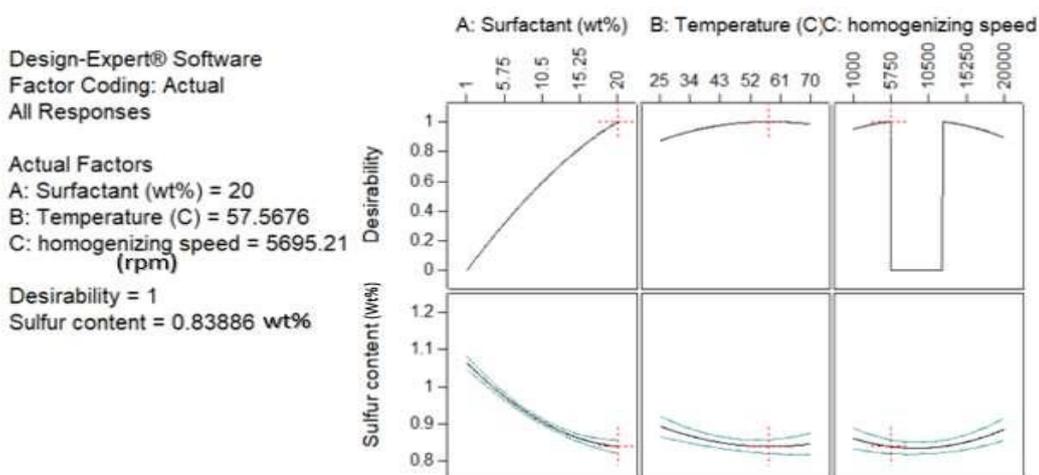
Fig. (2): Desirability and optimum result for EDS.

For the ADS the optimal results at desirability =1 showed that the sulfur content 0.57 wt% was achieved at the following conditions: adsorption time 7.18 hrs., temperature 53.3 °C, and clay mass 15.24 gm. The process desirability and optimization can be described in Figure (3). An increment

in adsorption time and clay mass positively affected the process, but temperature showed an adverse effect.
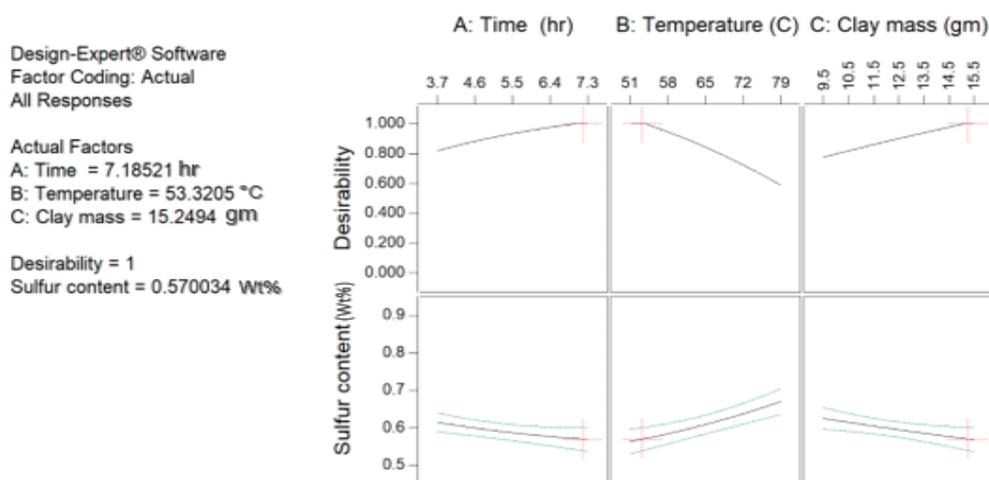
Fig. (3): Desirability and optimum result for ADS.

4.2 GC Characterization

Diesel fuel is characterized by GC analysis in each step of the desulfurization process to study the change in the sulfur compounds and the influence of desulfurization for each specific sulfur component as shown in Table (6).

The results of the desulfurization rate in each step are listed in Table 6. Some sulfur components such as BT, 3-methyl benzo-thiophene (3-MBT), dimethyl disulfide (DMDS), and 2-methyl-2-propaneth could be identified. For sulfur components, the rate of desulfurization varies in each phase. 2- Butanethiol has less sulfur component concentration, while 3-MBT has the highest sulfur concentration.

The ODS process completely reduces all sulfur components. The Diethyl disulfide (DEDS) recorded the highest desulfurization rate, 98.88%, and the lowest rate, 25.176%, for Thiophene.

Table (6) Desulfurization GC test for diesel in each step.

No.	Structure	Structure Name	Real Diesel Fuel (ppm)	ODS (ppm)	EDS (ppm)	ADS (ppm)
1		Dimethyl disulfide	0. 4074	0.0453	0.00	0.00
2		Diethyl disulfide	3.6393	0.0422	0.0709	0.00
3		2-Butanethiole	0.2433	0.1365	0.00	0.00
4		2-Methyl,2-propanethiole	0.8821	0.0632	0.00	0.00
5		Thiophene	90.6478	63.2831	0.3078	0.00
6		3-MT	152.9517	112.8237	1.0237	0.0381
7		BT	185.6382	138.9013	15.9742	1.8242
8		3-MBT	299.3178	192.2946	119.3899	28.1639
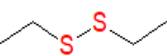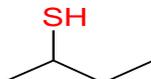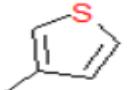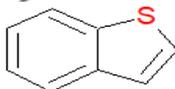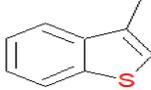
The EDS conducted a significant desulfurization rate for T, BT, and 3-methyl thiophene (3-MT). The oxidized sulfur components in the oxidation step are removed by the surfactant, where the remaining traces of DMDS, 2-butanethiol, and 2- 2-methyl-2-propanethiol are removed completely by the adsorption step. The highest rates for 3-MT and T desulfurization rated are 99.1% and 99.5%, respectively. The EDS is an effective process for removing the Thiophenes compounds.

The sulfur adsorption by clay identifies the definitive treatment. Most components have already been removed by the previous treatments, and this step is sufficient for removing the double-ring sulfur compounds BT and 3-MBT. Although the emulsification step recorded the highest desulfurization rate for Thiophene, this step can be defined as a finishing treatment for the

complicated sulfur compounds. The rates of desulfurization for BT and 3-MBT are 88.58% and 76.41%, respectively.

4.3 IREX Characterization

The properties of the fuel are determined at each stage of the desulfurization process, as shown in Table (7). Chemical reactions influence some aspects of the process at each stage. A higher quality diesel fuel may be obtained after the treatment operations. Emulsification and adsorption treatment can raise the cetane number (CN) of diesel fuel by lowering IBP and improving ignition quality. The Cetane Index (CI) then increased to 45.7 and 47.6 after emulsification extractive and adsorptive desulfurization, due to a decrease in IBP in these processes.

Table (7) IREX test in each desulfurization step.

NO.	Parameters	Diesel fuel	After oxidation	After Emulsification	After Adsorption
1	Cetane Number	46	45	49	51
2	Cetane index	43.3	39.4	45.7	47.6
3	Aromatics (Vol%)	27.1	9.2	2.1	11.7
4	PNA (Vol%)	4.3	4.5	7.0	4.7
5	FAME (Vol%)	0.00	1.72	0.00	0.00
6	Flashpoint (^{o}C)	68	72	75	78
7	IBP (^{o}C)	185.9	210	168.1	194.6
8	T10 (^{o}C)	229	241	307.1	208.9
9	T50 (^{o}C)	286.4	295.6	378.2	247.3
10	T90 (^{o}C)	329.6	312.9	402.2	332.3
11	EBP (^{o}C)	355.7	326	482.2	340.1

Following emulsification, there was a considerable increase in CN from 45 to 49, indicating a significant improvement. This rise in CN corresponds to a drop in aromatics from 27.1 to 2.1 vol.%. The higher polynuclear aromatic compound (PNA) after emulsification was found to be 7 vol%, compared to 4.3 and 4.5 vol% for diesel and oxidized diesel, respectively. As a result, the T50 and T90 in the distillation curve will be higher, at 378.2 and 402.2 ^{o}C, respectively.

During the adsorption process, the PNA was reduced to 4.7 vol%, raising the cetane number to 51. Furthermore, PNA reduction resulted in T50 and T90 distillation curves of 247.3 and 332.3 ^{o}C, respectively.

The presence of ester bonds formed by the reaction of the hydroxyl group (O-H) in hydrogen peroxide with the carbonyl group (C=O) in acetic acid that has a hydroxyl group (O-H) attached to the carbon atom resulted in the highest value of 1.72 vol% after oxidation of the diesel fuel.

5. Conclusions

1. RSM statistical analysis was used to enhance variables in emulsification and adsorption processes.

2. These desulfurization processes operate under mild conditions without using hydrogen and high facility costs.

3. The optimum condition for EDS is a surfactant concentration of 20 wt%, temperature of 57.56 ^{o}C, and homogenization speed of 5695 rpm.

4. The EDS is an active technique for removing T, BT, and 3-MT sulfur components. The desulfurization rates for 3-MT and T are 99.1% and 99.5%, respectively.

5. The optimum desulfurization condition by the adsorption process is adsorption time 7.18 hrs., temperature 53.3 $^{\circ}$C, clay mass 15.24 gm, and desirability =1.

6. The ADS is a significant process for removing the double-ring sulfur components. The desulfurization rate for BT and 3-MBT are 88.58% and 76.41%, respectively.

7. The diesel fuel quality (Cetane number, Flashpoint) is enhanced by EDS and ADS processes.

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