Preparation of Supported Bimetallic Ce/Fe activated carbon for Desulfurization reaction

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Abstract
Activated carbon is loaded with 2 totally different metals: Ce and iron. The catalyst was characterised by Brunauer Emmett Teller (BET) and Fourier rework Infrared (FTIR). The discharged conditioner had the best area and pore volume of 1100 m$^2$/g and 0.3 cm$^3$/g, respectively. AC/Ce/Fe achieved the best kerosene adsorption performance (75%) though the lowest surface area and pore volume of 965.7608 m$^2$/g and 0.39 cm$^3$/g due to the acidic sites required for adsorption of sulfur compounds. Batch experiments with AC/Ce/Fe showed a high adsorption capacity. These experiments were designed by Minitab Response Surface Methodology RSM 2019. The Analysis of variance ANOVA shows that the concentration of H$_2$O$_2$ has most significant effect on the sulfur removal followed by reaction time and temperature, respectively. The model optimization was set its parameters additives 10 ml H$_2$O$_2$, temperature 80 °C and time 5 hr.

Keywords: Activated carbon, Desulfurization, Response surface methodology, Sulfur removal.

1. Introduction
In recent years, rising global energy demand, stringent environmental legislation on transportation fuels and depleted oil reserves together have formed a triangle of constraints that pose significant challenges to refineries. Increased emissions in the form of SO$_X$ will increase with increased energy demand due to fuel combustion in transportation or in oil refineries.

These emissions are harmful because emitted sulfur dioxide (SO$_X$) can react with water in the atmosphere, forming acid rain that is harmful to soils, buildings, forests and ecosystems.
Sulfur emissions also exacerbate heart disease, respiratory diseases, cause asthma, and contribute to the formation of atmospheric particles.

Sulfur compounds in fuel oil, can be classified into four main groups mercaptans, thiophenes (TH), benzothiophenes (BT), and dibenzothiophenes (DBT) [1].

Crude oil and distillated petroleum contain undesirable sulfur due to the following reasons:

- Organic sulfur compounds can cause the emission of sulfur oxides (SO$_X$) as a result of the combustion of fuel used in transportation, which leads to acid rain.
- Many corrosion problems occur in pipes, pumps, and other refining units due to sulfur compounds. Sulfur emissions also cause respiratory diseases, exacerbate heart disease, cause asthma and contribute to the formation of atmospheric particles.
- In reforming process, organic sulfur compounds caused poisoning for the catalyst.
- Organic sulfur compounds cause premature failures for combustion engines and poison the chemical action converters that are employed in automotive engines and alternative industrial operations.

As a result, environmental regulations on the sulfur level are legislated in transportation fuels in recent years, that have reduced the sulfur content in diesel to less than 10 ppm since 2005 in Europe, less than 15 ppm since 2006 in the US, and less than 50 ppm since 2008 in Beijing and Shanghai in China.

Therefore, fuel desulfurization may be a terribly necessary method within the oil industry, and there’s a necessity to search out new strategies that are a lot of economical and efficient and meet the expectations of environmental rules and purification requirements. many methods are applied to get rid of sulfur compounds from fuel oil, like hydrodesulfurization (HDS), extractive distillation, selective adsorption, bio desulfurization, and oxidative desulfurization (ODS).

ODS is taken into account a promising desulfurization technology as a result of it is operated at temperature and low and doesn't need the employment of hydrogen. Also, ODS will simply take away the refractory sulfur compounds due to their high lepton density. ODS method can enhance the potency of sulfur removal while not destroying and poisoning catalyst[3].
On the contrary, acetonitrile has good physical properties such as low boiling point (82°C), so the separation of sulfones is easily achieved by distillation process[4].

**Gao et al. (2018)** studied the oxidative desulfurization process of a model fuel using oxygen as an oxidizer and CNTs/MOF-199-Mo16V2 as a catalyst. The test results indicate that the CNTs/MOF-199-Mo16V2 catalyst possesses superior catalytic activity, with a desulfurization efficiency of 98.30% obtained. Also, the CNTs/MOF-199-Mo16V2 shows excellent reusability and the catalytic efficiency is slightly reduced after 7 times recycling [5].

**Ghubayra et al. (2019)** studied the (ODS) process of diesel fuel using H2O2 as an oxidant and heteropoly acids supported on activated carbon (HPA/C) as a catalyst. The results showed that the catalytic activity of HPA/C were found to decrease in the order of HPA: H3PMo12O40>H3PW12O40 >H4SiW12O40. The most active catalyst is H3PMo12O40/C and has exhibited 100% of benzothiophenes (BT) removal from diesel fuel at 60 °C [6].

**Wang et al. (2019)** worked on the oxidation of DBT in model diesel cut using tungsten trioxide immobilized on carbon nanotubes (WO3/CNT) as a catalyst and hydrogen peroxide (H2O2) as an oxidant. It was found that the removal of dibenzothiophene (DBT) reached 90.73% after 60min [7].

**Ye et al. (2020)** investigated the catalytic performance of MoOx/CN for ODS of model diesel cut containing DBT as a sulfur compound. It was found that the MoOx/CN catalyst showed very excellent performance of ODS towards DBT. The highest desulfurization efficiency reached 99.9% and the sulfur content was eliminated from 800ppm to 10ppm. [8].

**Rezvani et al. (2019)** studied the performance of Fe2^5W18Fe4^4/FeTiO3 nanocomposite catalyst for ODS of model fuel containing TH, BT and DBT using peroxyacetic acid as the oxidant. The results indicated that the removal efficiency of DBT, BT and TH were achieved to be 97, 98, and 99%, respectively. Also, the evaluation of reusability of the heterogeneous nanocatalyst showed that the Fe2W18Fe4^4/FeTiO3 could be reused up to five runs conveniently [9].

**Ammar et al. (2018)** Magnetic CuO-Fe3O4 nanocomposites were prepared by simple impregnation method as photo-oxidative desulfurization catalyst for typical fuels (dibenzothiophene, DBT in n-hexane) and real naphtha under mild conditions. The typical fuel treatment results showed that the prepared nanocomposite can eliminate 95.2% of DBT
after 120 minutes under the following conditions: CuO:Fe₃O₄ weight ratio 1:1, catalyst dose 10g/L, H₂O₂/DBT molecule ratio 7.5:1 and DBT concentration Initial 250 mg/L [10].

Muhammad et al. (2018) Investigation of the oxidation of DBT using Fe, its fusing with Co or Ni based Mo/Al₂O₃ catalysts and (H₂O₂ and formic acid) as oxidizers. The results showed that 99% of the DBT conversion was achieved at 60 °C and 150 min reaction time on Fe-Ni-Mo/Al₂O₃. Also, iron significantly enhanced the ODS activity of Mo/Al₂O₃ based Co or Ni catalysts and took the following activity order: Fe–Ni–Mo/Al₂O₃ > Fe–Co–Mo/Al₂O₃ > Ni–Mo/Al₂O₃ > Co–Mo/Al₂O₃[11].

Subhan et al. (2019) The ODS of DBT was studied at room temperature over low-temperature Mn (0.5% by weight) in which Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts were combined using NaClO as the oxidant. The results showed that a very high and rapid 100% DBT conversion was achieved within 5 minutes, 0.1 mL of 0.138 mol NaCl (O/S- 6.6 mol/mol), 0.1 g Mn-Co-Mo/Al₂O₃ catalyst at pH 12. The reaction temperature is 25°C. The overall catalytic activity of ozone-depleting substances was arranged as follows: Mn–Co–Mo/Al₂O₃>Mn–Ni–Mo/Al₂O₃>Co–Mo/Al₂O₃>Ni–Mo/Al₂O₃>Mo/Al₂O₃ observed [12].

2. Experimental Work

Materials and chemicals

2.1. Oil feedstock

Kerosene is used as a feedstock with sulfur content (0.2244 wt. %) supplied by the Midland refinery /Al-Dura refinery. The physical properties of the Kerosene are illustrated in Table (1).

| Physical property          | Value        |
|----------------------------|--------------|
| Sulfur content(ppm)        | 2244.4       |
| Flash point (°C)           | 51.2         |
| Density(g/cm³)             | 0.817        |
| Boiling point (°C)         | 156.2-237.3  |
2.2. Catalysts
Activated carbon AC used in the present work, mean partial size of AC was 300 mesh (0.048 mm). The AC dried in an oven at 110 °C for 4 h to remove any moisture and stored in a desiccator. It was supplied by Central Drug House, India to the Iraqi local markets.

2.3. Chemicals
The chemical compounds that used in this study are listed in Table (2):

| Chemicals          | Formula                | Molecular Weight g/mol | Purity %  | Supplier       |
|--------------------|------------------------|------------------------|-----------|----------------|
| Ethanol            | C_2H_5OH               | 46.07                  | 99.9%     | Scharlab       |
| Ethylene glycol    | C_2H_4(OH)_2           | 62.07                  | 99%       | Thomas Baker   |
| Cerium nitrate hexahydrate | Ce (NO_3)_3.6H_2O  | 434.22                  | 99.9%     | ALFA Chemistry |
| Ferric nitrate nanohydrate | Fe(NO_3)_3.9H_2O | 404                     | 97-102%   | Himedia        |
| Hydrogen Peroxide  | H_2O_2                 | 34.01                  | --        | Germany        |

2.4. Catalyst preparation:

Loading cerium and iron bimetallic composite on AC (AC/Ce/Fe)

1–7.0 g AC was dispersed in 150 ml deionized water, 100 ml ethanol, 20 ml ethylene glycol, and stirred for 20 min at 60% capacity and 1,000,000 J by a sonic device.

2- Next, a 5 ml solution containing 0.88 g of cerium nitrate hexahydrate solution was added dropwise into dispersed AC and maintained at pH 8-9. The mixture was reflowed at 90 °C for 2 h. And leave it until the second day.

3- The precipitate was washed and dried at 110°C, 18 hours.

4- The desiccant was dispersed in 150 mL deionized water, 100 mL ethanol, and 20 mL ethylene glycol by sonicator for 20 min at a capacity of 60% and 1,000,000 J.
5- A 13 ml solution containing 5.06 g of iron nitrate was added dropwise to the mixture and maintained at pH 8-9.

6- Re-flow the air at 90°C, 330 rpm for 2 hours, leave until the second day.

7- The precipitate was filtered, washed and dried at 110°C in an oven for 18 hours to remove water and salt crystallization at the pore surface.

8- The dried catalyst was calcined at 350 °C in an oven for 4 h to ensure that the metals were adequately localized on the surface of the air conditioner.

2.5. Experimental Design

In this work, the experimental work includes carrying out different experiments process by using the following operating conditions:

1- Reaction time (2, 5 and 24) hr.
2- Reaction Temperature (25, 50, and 80) ºC.
3- Amount of H₂O₂ (0, 1, 5, and 10) ml.

2.6. Oxidative Desulfurization Process Batch Reactor

The oxidisation reaction of the sulfur compound is applied during a batch reactor. A fifty ml single-neck circular flask is employed for the reaction. The neck is connected to a vertical condenser to condense fuel vapor. The round flask is placed round the neck on a beaker full of water to confirm even heat distribution. A thermometer is placed to measure the temperature. The batch reactor is heated and mixed by a magnetic stirrer.

3.7. Oxidation of Sulfur Experimental Procedure

The raw material for oil is kerosene containing sulfur compound. The following steps are performed in each run:

1. 25 mL of feedstock is shipped to the round bottom flask along with 0.5 g of catalyst.
2. A specified amount of hydrogen peroxide is added.
3. The flask was placed in the heating mantle motor and connected to the condenser. The flow of cooling water through the condenser is ensured to prevent any evaporation of kerosene. A thermometer is inserted to measure the reaction temperature.
4. When the required time is achieved, the amount of kerosene is withdrawn.
5. The withdrawn amount was allowed to settle in a separating funnel where clearly distinguishable phases were obtained. Then the sample was withdrawn from the organic phase.

6. At the end of the operation, the heating mantle motor was turned off and the product material was filtered.

7. The sulfur content was tested in all the drawn samples.

4. Results and Discussions

4.1 Catalysts Characterization

The textural characteristics of the original and modified activated carbon are presented in Table (3).

| Type of AC  | SA (m²/g) | PV (cm³/g) | BD (g/cm³) | RD (g/cm³) | Porosity |
|------------|-----------|------------|------------|------------|----------|
| Parent AC  | 1069      | 0.627      | 0.69       | 1.9927     | 0.6537   |
| Ce-Fe/AC   | 965.7608  | 0.3943     | 0.56       | 2.342      | 0.76088  |

4.2 FTIR

The FTIR spectra of all the adsorbents are appeared in Figure (1). To get it what kind of utilitarian bunches are on the adsorbent, and to screen whether there are likenesses within the relative thickness of each utilitarian bunch. Each retentive appeared changing degrees of the relative force of the utilitarian bunches, but they all appeared a comparative design. The crests at 1400 cm⁻¹ and 2200-2400 cm⁻¹ are relegated to the C = O extending vibrations and the double-bonded carbon and oxygen bunches [13]. The final crest that showed up at 1020 cm⁻¹ was credited to the C–O extending vibration. These crests are the properties of undefined carbon, hence, the reason why simply synthesized AC gave the most noteworthy escalation. Be that as it may, the escalated of the crests diminished upon metallic stacking to bolster the comes about gotten from Wagered, XRD, and SEM. The result affirms the affiliation of the oxygen-containing useful bunches with the nanoparticles. The top at 550.84 cm⁻¹ shows the nearness of Ce–O inside the AC/Ce test, but it does not show up within the
AC/Ce/Fe since the concentration of Ce in that adsorbent was irrelevant. The extend that showed up around 1020 cm\(^{-1}\) is for the Ce–O–C. response \[14\][15]. The little crests that showed up at 798 and 895 cm\(^{-1}\) were credited to Fe-O bowing vibrations, whereas the crests at 624 cm\(^{-1}\) were due to Fe-O extending vibrations inside AC/Fe and AC/Ce/Fe \[16\][17].

![FTIR spectrum of AC; and AC/Ce, AC/Fe, and AC/Ce/Fe](image)

**Fig. (1):** FTIR spectrum of AC; and AC/Ce, AC/Fe, and AC/Ce/Fe

### 4.3 Effect of Amount of Hydrogen Peroxide

Diverse sums of \(\text{H}_2\text{O}_2\) (0, 1, 5, 10) ml were included to 25 ml of lamp fuel at diverse temperatures (25, 50, and 80) °C at a steady motor speed of 330 rpm and a consistent time of 5 h. As appeared in Figure (2), it has been found that the evacuation proficiency of sulfur compounds increments with an expanding sum of \(\text{H}_2\text{O}_2\) to a certain point. It may well be clarified that the critical increase in hydrogen peroxide, on the one hand, may well be ascribed to the warm decay amid the response ascribed to the work of the oxidizer in changing over the sulfur compound into sulfoxides and/or sulfonates. These comes about are
well concurred with Li et al. 2013 [18]. It was observed that at 80 °C and using 10 ml of H₂O₂ an increase in desulfurization was obtained. Therefore, it can be concluded that increasing the amount of H₂O₂ with increasing temperature had a more pronounced effect resulting in more sulfur removal to about 75%.

![Graph](image)

**Fig. (2):** The effect of amount of H₂O₂ on sulfur removal at different temperatures, 330 rpm, 5 hr.

### 4.4 Effect of Reaction Temperature

The impact of response temperature on desulfurization effectiveness was explored for 5 h response time at 25°C, 50°C, and 80°C utilizing distinctive sums of hydrogen peroxide; (0, 1, 5, and 10) ml as appeared in Figure (3). The gotten comes about demonstrated that the oxidation of thiophene compounds and their subsidiaries was upgraded to sulfone oxide and sulfonate when the response temperature was expanded from 25°C to 80°C and the desulfurization proficiency was made strides. As seen at 25°C, desulfurization was underneath 50°C and 80°C. Expanding the response temperature improves the oxidation of lamp fuel. This may be related to the deterioration of hydrogen peroxide in parallel with an increment within the response, temperature creates hydroxyl radicals that act as a solid oxidizing specialist. The same behavior has moreover been watched by a few analysts, such as Lanju et al., 2006[19].
4.5 Effect of Reaction Time

Figure (4) appears desulfurization as a work of response time at working temperature 25°C and 80°C, sum of H2O2 10 ml. The comes about are made strides by expanding the response time. This response, like several other responses, needs sufficient time to complete and fortify over time. The finest comes about are watched inside 5 hours [20]. Similar behavior was obtained by Yanxiu et al., 2013 [21] for the oxidative desulfurization of a normal sulfur compound by the nearness of a phosphorous molybdic corrosive catalyst in which the remaining sulfur substance was found to diminish with expanding oxidation time. The response was near to harmony and the leftover sulfur substance was nearly unaltered.

4.6 Optimization Design by Using Response Surface Methodology

To investigate the intuitive impacts of parameters on desulfurization, reaction surface technique (RSM) was utilized to optimize the impacts of H2O2 concentration, temperature,
and time on desulfurization. The plan of tests was performed in an RSM plan called the Central Composite Plan (CCD). Desulfurization was chosen in reaction to these variables. Table (4) appears the levels and ranges coded for the working factors. The values encoded for the components were utilized to smooth the relapse with +1 as the most extreme level and -1 as the most reduced. In add up to, 20 exploratory bunches are appeared in Table (5), comprising of eight fragmentary components (2 k), six pivotal runs (2 k), and three duplicates outlined at the center point, whereas k was the number of variables.

Table (4) Experimental Design for Desulfurization, Their Coded and Actual Levels.

| Factors          | Coded Levels |
|------------------|--------------|
|                  | -1           | 1             |
| A: Temperature °C | 25           | 80            |
| B: Concentration of H2O2 ml | 0           | 10            |
| C: time hr       | 1            | 48            |

Table (5) Factors and Response Values of Sulfur Removal.

| Run | Factor 1 Temperature °C | Factor 2 Concentration of H2O2 ml | Factor 3 Time hr | Response Sulfur Removal % |
|-----|-------------------------|----------------------------------|------------------|--------------------------|
| 1   | 25                      | 1                                | 2                | 29.8968                  |
| 2   | 25                      | 1                                | 4                | 28.0242                  |
| 3   | 25                      | 1                                | 48               | 47.7222                  |
| 4   | 80                      | 1                                | 2                | 32.1319                  |
| 5   | 80                      | 1                                | 5                | 31.7224                  |
| 6   | 80                      | 1                                | 24               | 33.6248                  |
| 7   | 50                      | 1                                | 2                | 32.0508                  |
| 8   | 50                      | 1                                | 5                | 35.8343                  |
| 9   | 50                      | 1                                | 24               | 41.5714                  |
| 10  | 80                      | 0                                | 1                | 24.0787                  |
| 11  | 80                      | 0                                | 2                | 24.0275                  |
Reaction values were recorded from the comes about of desulfurization tests extending from 19% to 75%. An ANOVA investigation is displayed in Table (6), showing that the desulfurization reaction surface with R2 esteem of 0.974 appeared that 97.4% of the contrasts that happened for desulfurization were clarified by the proposed demonstrate. The closing values for R2 (0.974) and balanced R2 (0.9506) demonstrated that the proposed show was reasonable for foreseeing desulfurization effectiveness.

Table (6) ANOVA results of the reduced quadratic model for the sulfur removal efficiency.

| Source   | DF | Adj SS    | Adj MS    | F-Value | P-Value |
|----------|----|-----------|-----------|---------|---------|
| Model    | 9  | 5219.97   | 579.996   | 62.02   | 0       |
| Linear   | 3  | 1273.87   | 424.623   | 45.41   | 0       |
| A        | 1  | 9.32      | 9.317     | 1.00    | 0.34    |
| B        | 1  | 254.43    | 254.427   | 27.21   | 0       |
| C        | 1  | 0         | 0.002     | 0       | 0.988   |
| Square   | 3  | 384.91    | 128.302   | 13.72   | 0       |
| A²       | 1  | 0.54      | 0.539     | 0.06    | 0.815   |
| B²       | 1  | 211.54    | 211.543   | 22.62   | 0.001   |
| C²       | 1  | 27.11     | 27.111    | 2.9     | 0.117   |
| Way Interaction | 3  | 304.50 | 101.499   | 10.85   | 0.001   |
The polynomial quadratic condition in terms of values encoded to anticipate desulfurization effectiveness is displayed in condition (1), where $y$ is the reaction figure to desulfurization. The condition appears that the straight variables of the A and C interaction and the AC interaction have positive impacts on the reaction, whereas the negative coefficients demonstrate unfavorable impacts on the desulfurization effectiveness.

Regression Equation in Uncoded Units

\[
\text{conv.} = 22.35 + 0.040 \text{Temp.} + 6.65 \text{conc.H}_2\text{O}_2 + 1.484 \text{time} - 0.00066 \text{Temp.}^2 - 0.506 \text{conc.H}_2\text{O}_2 \times \text{conc.H}_2\text{O}_2 - 0.01650 \text{time} \times \text{time} \\
+ 0.04494 \text{Temp.} \times \text{conc.H}_2\text{O}_2 - 0.01269 \text{Temp.} \times \text{time} - 0.0026 \text{conc.H}_2\text{O}_2 \times \text{time}
\]

The effects of the interaction of two agents on desulfurization were illustrated by two-dimensional contour plots of the three-dimensional response surface, as shown in Figure (5). Desulfurization was more sensitive to H$_2$O$_2$ concentration and temperature than the time. The desulfurization increased at HO concentration as shown in Figure (5)(b) when the temperature and time were fixed at 80 °C and 24.5 h, respectively. Increasing the H$_2$O$_2$ concentration, the desulfurization was increased from 19% to 75%. Desulfurization increased first and then decreased with increasing temperature, as shown in Figure (5)(c). However, the H$_2$O$_2$ dose ranging from 0 to 10 mL is more sensitive to being affected by desulfurization, as shown in Figure (5)(e). The numerical optimization was performed using maximum desulfurization, lowest concentration of H$_2$O$_2$, and lower consumption of the catalyst. The best desulfurization was 75% under conditions of 10 ml, 80 °C and 5 h. The efficiency of the analysis model was more than 97%.
Fig. (5): The 3D response surface and 2D contour plots for the interaction effects on the sulfur removal. In (a,b) Temperature = 80°C; in (c,d), Dosage. H₂O₂ = 10 m; and in (e,f), time = 5 h.
5. Conclusion

1) The main activated carbon Ce-Fe/AC and all treatments (H₂O₂ dose, temperature and time) showed activity of varying degrees to remove sulfur compounds from kerosene, and the effective sequence is as follows:
Temperature > H₂O₂ Dosage > Time > Origin Ce-Fe/AC

2) The oxidative desulfurization efficiency of simulating kerosene increases with the increase; Temperature and acidity of the reaction mixture and the dose of H₂O₂. The maximum desulfurization efficiency reached 75%, and was achieved at; T = 80 °C, t = 5 h. H₂O₂ dose = 10 ml.

3) Operating variables on desulfurization efficiency were improved through the use of a response surface methodology. The efficiency of the analysis model was more than 97% under optimal conditions: temperature 80 °C, dose of H₂O₂ 10 ml and time 5 hours.
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