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# Catalytic oxidative desulfurization of diesel utilizing hydrogen peroxide and functionalized-activated carbon in a biphasic diesel–acetonitrile system

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ABSTRACT

This paper presents the development of granular functionalized-activated carbon as catalysts in the catalytic oxidative desulfurization (Cat-ODS) of commercial Malaysian diesel using hydrogen peroxide as oxidant. Granular functionalized-activated carbon was prepared from oil palm shell using phosphoric acid activation method and carbonized at 500 °C and 700 °C for 1 h. The activated carbons were characterized using various analytical techniques to study the chemistry underlying the preparation and calcination treatment. Nitrogen adsorption/desorption isotherms exhibited the characteristic of microporous structure with some contribution of mesopore property. The Fourier Transform Infrared Spectroscopy results showed that higher activation temperature leads to fewer surface functional groups due to thermal decomposition. Micrograph from Field Emission Scanning Electron Microscope showed that activation at 700 °C creates orderly and well developed pores. Furthermore, X-ray Diffraction patterns revealed that pyrolysis has converted crystalline cellulose structure of oil palm shell to amorphous carbon structure. The influence of the reaction temperature, the oxidation duration, the solvent, and the oxidant/sulfur molar ratio were examined. The rates of the catalytic oxidative desulfurization reaction were found to increase with the temperature, and $H_2O_2$/S molar ratio. Under the best operating condition for the catalytic oxidative desulfurization: temperature 50 °C, atmospheric pressure, 0.5 g activated carbon, 3 mol ratio of hydrogen peroxide to sulfur, 2 mol ratio of acetic acid to sulfur, 3 oxidation cycles with 1 h for each cycle using acetonitrile as extraction solvent, the sulfur content in diesel was reduced from 2189 ppm to 190 ppm with 91.3% of total sulfur removed.

## 1. Introduction

Catalytic oxidative desulfurization (Cat-ODS), as an alternative to the conventional hydrodesulfurization (HDS), is regarded as the most promising and economical process to meet the future environmental regulation with low sulfur diesel or even sulfur free diesel. Various studies on the Cat-ODS process have employed different systems, including the combination of $H_2O_2$ with organic acid (such as formic acid, acetic acid and heteropolyacid) [1–4], polyoxometallic acid [5] or amphiphilic peroxotungsten emulsion catalyst [6]. Acetic acid was known to act as a co-catalyst which provides the acidic medium [1] for Cat-ODS process and stabilizes hydrogen peroxide [2] by forming peroxyacetic acid which is more stable at higher reaction temperature, thus, minimize the decomposition of hydrogen peroxide to other side products such as water and oxygen. So, more peroxy groups can be supplied on the catalyst surface for the oxidation of sulfur compounds [2]. Hence, the presence of acetic acid in the reaction can further promote the oxidative activity of hydrogen peroxide in Cat-ODS process. The Cat-ODS was further enhanced with the presence of tetrapropylammonium bromide which acts as phase transfer agent that facilitates the transfer of reactants and products between polar–apolar interfaces. Chemical activation of various carbon materials by phosphoric acid has long been known and widely used for the preparation of activated carbon. Phosphoric acid is a Brönsted acid and a strong dehydrating agent, thus being more effective to induce depolymerization, dehydration and redistribution of constituent biopolymers in the pyrolytic decomposition of the resulting carbon materials [7]. The greatest advantage of the phosphoric activation is that it allows the development of both micropores and mesopores on the prepared activated carbon [8,9]. Activated carbon can be directly used as catalyst or catalyst support in a heterogeneous catalysis which contributes to its wide applications such as drinking water [10,11] and waste water treatments [12], desulfurization of fuel [1,13,14], pharmaceutical [15,16], food [17], beverage and chemical industries [18].

Activated carbon has long been used as an effective heterogeneous catalyst in $H_2O_2$ decomposition to form hydroxyl radicals which

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is a powerful oxidant [19]. In Cat-ODS process, the hydroxyl radicals reacted with organic acids to form peracids and oxidized the organosulfur compounds to their corresponding sulfoxides and sulfones. The ongoing research, currently involved the development of functionalized-activated carbon as catalyst in Cat-ODS process for the production of low sulfur diesel fuel. Limited work has been reported on the studies of activated carbon as catalyst in Cat-ODS. Numerous studies had focused on using coal and wood-based activated carbon as the adsorptive carbon source [20–28]. Yu et al. [1] had studied on a ODS process which involved the combination of oxidation and adsorption process. The researchers used commercial powder activated carbon as catalyst and adsorbent, formic acid as co-catalyst and hydrogen peroxide as oxidant for the treatment of diesel fuel with 800 ppm of sulfur content. The researchers managed to diminish the sulfur content to 16 ppm with 98% of total sulfur removal after 12 h adsorption by activated carbon. In this work, we focus on developing a cost effective catalytic oxidative desulfurization process by preparing and utilizing granular functionalized-oil palm shell-based, phosphoric acid-activated carbon as catalyst together with hydrogen peroxide as oxidant and acetonitrile as extraction solvent to produce diesel fuel which complies with the Euro 3 standard.

## 2. Experimental

### 2.1. Reaction reagents

All solvents and reactants were obtained from Aldrich and used without further purification: hydrogen peroxide solution 30%, acetonitrile 99.9%, tetrapropylammonium bromide 99%, glacial acetic acid 99%, and phosphoric acid solution 85%. The fuel tested was a commercial Malaysian (Petronas) diesel fuel with 2189 ppmw sulfur. The raw oil palm shell was obtained from an oil palm mill located in Kulai, Johor, Malaysia.

### 2.2. Preparation of functionalized-activated carbon

The activated carbon was synthesized by phosphoric acid activation method and the typical preparation steps were performed as follows: 100 g of oil palm shell was repeatedly washed with tap water until all dust particles were removed and dried in an electrical oven. The dried material was pre-treated by soaking it in 30 wt.% phosphoric acid solution for 24 h. After that, the oil palm shell was thoroughly washed with distilled water and dried in an electrical oven. The dried material was then impregnated with 85 wt.% phosphoric acid solution for 20 h. The impregnated oil palm shell was dried in an electrical oven at 110 °C for 24 h. The oil palm shell was then carbonized in a muffle furnace for 1 h at 500 °C and 700 °C. The activated carbon was then repeatedly washed with distilled water until the pH of the solution is close to the initial pH of the rinsing water. Finally, the activated carbon was dried in an electrical oven at 110 °C for 24 h. The activated carbon calcined at 500 °C and 700 °C were labeled as AC-500 and AC-700, respectively.

### 2.3. Characterization of functionalized-activated carbon

The physical properties of the prepared activated carbon were studied by nitrogen adsorption/desorption measurement, X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscope (FESEM) and Thermogravimetric analysis (TGA). $N_2$ adsorption/desorption isotherm of the catalysts was obtained using Micromeritics ASAP 2010 volumetric adsorption analyzer at −196 °C. Prior to the measurement, the calcined catalysts were degassed at 200 °C overnight. The isotherms were used to determine the following parameters: surface area [using Brunauer–Emmett–Teller (BET) equation], total pore volume, total micropore volume, and total mesopore volume. The XRD patterns of the prepared activated carbon powder samples were recorded at $2\theta$ between 5° to 75° using a Bruker Advance D8 with Siemens 5000 diffractometer. The Cu $K_\alpha$ radiation operates at 40 kV and 40 mA with $\lambda = 1.5418$ Å. The FTIR spectra were recorded using a Perkin Elmer Spectrum One spectrometer with a resolution of 4 $cm^{-1}$ and 5 scans in the mid IR region (400–4000 $cm^{-1}$). The surface morphology of the samples was analyzed using Zeiss Supra 35VP FESEM with the energy of 15.0 kV and 1500× magnification. Prior to the analysis, the sprinkled sample was coated with gold as conducting material by gold sputter at $10^{-1}$ Mbar using Bio Rad Polaron Division SEM coating system machine. TGA analysis for the samples was carried out by TGA-SDTA 851 Mettler Toledo simultaneous thermal analyzer up to 800 °C at 15 °C/min. The sample in the form of fine powder was placed in an alumina covered crucible, an empty crucible being the reference. Nitrogen gas with the flow rate of 50 µL/min was used as the atmosphere.

### 2.4. Catalytic tests

A typical experiment was performed as follows: In a 100 mL round-bottom flask equipped with a magnetic stirrer and a heated circulating bath, 50 mL of diesel fuel was mixed with an appropriate volume of a solution containing glacial acetic acid 99% with 2 mol of acetic acid to sulfur ratio, hydrogen peroxide 30 wt.%, 0.5 g of tetrapropylammonium bromide, and 0.5 g of functionalized-activated carbon at 50 °C and atmospheric pressure. The mixture was refluxed for 1 h under vigorous stirring. After the reaction, the oxidized diesel fuel was extracted by 10 mL acetonitrile with a solvent: oil volume ratio = 1:5. The extraction process was carried out in a conical flask equipped with a magnetic stirrer. The mixture of diesel and acetonitrile was vigorously stirred for 30 min at room temperature followed by phase separation in a separating funnel, and left until two separate layers of diesel and solvent formed. A similar extraction step was repeated for the next two extraction cycles. After the extraction, the diesel layers were collected and analyzed for sulfur content by XRF spectroscopy (ASTM D-4294) and Gas Chromatography with Flame Photometric Detector (GC-FPD). The efficiency of the desulfurization process was measured based on various reaction parameters such as the oxidant concentration, oxidation duration, reaction temperature, different types of catalysts and extraction solvent, and multiple oxidation cycles.

The adsorptive test for the prepared activated carbon was conducted in a similar reactor system used for the catalytic testing. 0.5 g of the activated carbon was added to a round-bottomed flask containing 50 mL diesel. The mixture was then refluxed at 50 °C and atmospheric pressure for 3 h under vigorous stirring. Samples were withdrawn at different time interval, filtered with 0.45 µm micro filter and then analyzed by XRF spectroscopy and GC-FPD for sulfur content.

## 3. Results and discussion

### 3.1. Characterization of catalyst

Yields of oil palm shell activated carbon used in this study were found to be 33.25% and 27.38% for AC-500 and AC-700, respectively. The yield was calculated as the final weight of the activated carbon produced after activation, washing, and drying, divided by the initial weight of oil palm shell; both on a dry basis [29]. Pore characteristic of the oil palm shell activated carbon was determined by $N_2$ adsorption/desorption measurement as illustrated in Fig. 1. Both treated AC-500 and AC-700 activated carbons possess Type I IUPAC isotherm, indicating the presence of micropores. Besides that, the existence of the hysteresis loop indicated that some mesopore property was also presence. Both isotherms exhibited type H4 hysteresis loop, characteristic of slit-shaped pores. The presence of micropores and mesopores in the activated carbon prepared from oil palm shell was

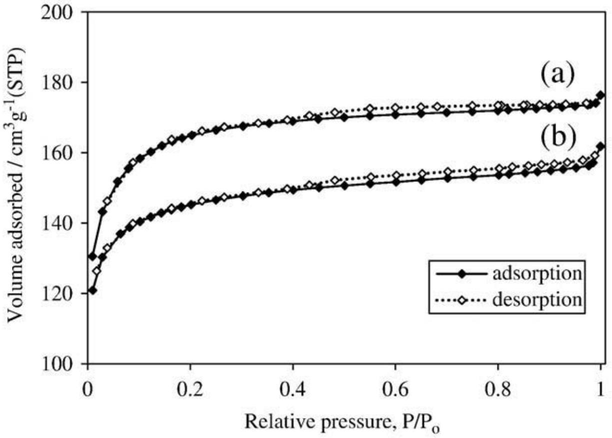


**Fig. 1.** Nitrogen adsorption/desorption isotherm of: (a) AC-700, and (b) AC-500.

also indicated by the pore size distribution as depicted in Fig. 2. As shown in the figure, both AC-500 and AC-700 activated carbons consist mainly of micropore with minor mesoporosity. In this study, the activated carbon synthesized was calcined in the range of 500 °C to 700 °C. Based on the previous study, calcination below 500 °C still shows the existence of foreign species on the activated carbon. Besides that, activation below 500 °C leads to incomplete carbonization and lower surface area of the material. Calcination at temperature above 700 °C will eliminate most of the required surface functional groups due to thermal decomposition.

Table 1 shows the pore characteristics of oil palm shell activated carbon. AC-700 showed higher BET surface area (560 m$^2$ g$^{-1}$) than AC-500 (489 m$^2$ g$^{-1}$). This was probably due to higher activation temperature with higher burn-off, creating more porous structure with higher pore volume on the surface.

**Table 1**
Porous structure of AC.

| Samples | $S_{BET}$ (m$^2$ g$^{-1}$) | $V_{Total}$ (cm$^3$ g$^{-1}$) | $V_{Micro}$ (cm$^3$ g$^{-1}$) | Average pore diameter, $W_d$ (Å) |
|---|---|---|---|---|
| AC-500 | 489 | 0.24 | 0.18 | 19.7 |
| AC-700 | 560 | 0.27 | 0.19 | 19.1 |

Fig. 3 shows the infrared spectra for functionalized-activated carbons and oil palm shell. For the oil palm shell, the peaks around 1400 and 1300 cm$^{-1}$ were attributed to the aromatic C–H and carboxyl-carbonate structures and the peak at around 1036 cm$^{-1}$ corresponds to C–O stretching of C–OH group [30]. The broad peak at around 3410 cm$^{-1}$ was due to the –OH stretching of hydroxyl groups and adsorbed water. For both functionalized-activated carbons, the peak at 1036 cm$^{-1}$ was nearly diminished. This is because during the phosphoric acid activation, the hydroxyl groups are converted into acidic oxygen-containing groups on the carbon surface. For AC-500, the band around 1565 cm$^{-1}$ was assigned to the vibration of the C–O stretching of carbonyl group [30]. The peak at 1240–1150 cm$^{-1}$ may be ascribed to the stretching mode of hydrogen bonded P O, and P OOH; and the shoulder at 1042 cm$^{-1}$ can be ascribed to O–C stretching vibrations in P–O–C linkage [30–32]. The spectrum of AC-700 showed fewer peaks with low intensity, indicative of comparatively less amount of surface functional groups due to decomposition at high temperature.

Fig. 4 shows the FESEM micrographs of AC-500 and AC-700. It was obvious that the activated carbon produced have cavities on their external surface which resulted from the evaporation of phosphoric acid during carbonization. The FESEM micrograph for AC-500 showed smooth surface with uneven distribution of pores (Fig. 4a) while AC-700 showed ordered and well developed pores which covered evenly over the surface, thus possess higher BET surface area (Fig. 4b).

Fig. 5a shows the thermal stability profile of oil palm shell investigated by thermogravimetric analysis (TGA). A small weight loss at ambient temperature to 150 °C was assigned to the release of moisture. A weight loss of approximately 33% in the range of 200 °C to 350 °C was probably due to the surface hydroxyl condensation process and decomposition of phosphoric species. The remaining gradual weight loss was due to the hydroxyl group condensation. Results from differential thermal analysis (DTA) showed that exothermic process occurs between 200 °C to 350 °C which was assigned to the transformation of cellular to amorphous structure (Fig. 5b).

Fig. 6 shows the XRD patterns of AC-500 and AC-700. For both activated carbons, the diffraction profiles exhibited broad peaks at 2$\theta$ around 24° and 42° was assigned to the reflection from (002) and (10) planes, respectively [33]. The appearance of a broad peak between 15° and 35° 2$\theta$ diffraction indicated the presence of silica with amorphous structure [34,35]. Higher pyrolysis temperatures resulted in expansion and disruption of cellular structure, creating a predominantly amorphous structure [36]. According to Walde et al. [37], the presence of a small peak at a *d*-spacing of 3.4 Å (26° 2$\theta$) indicates the transformation of polymeric oil palm shell to graphitic carbon.

### 3.2. Catalytic evaluation

Fig. 7 shows the effect of hydrogen peroxide concentration on sulfur elimination. Four $H_2O_2$-to-sulfur molar ratios were tested,

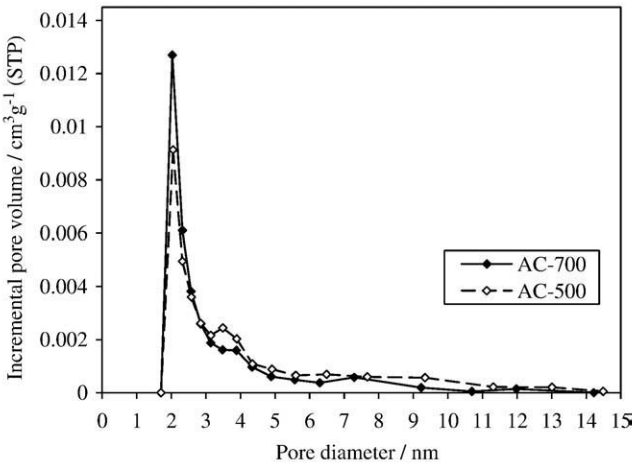


**Fig. 2.** Pore size distribution of oil palm shell activated carbon.

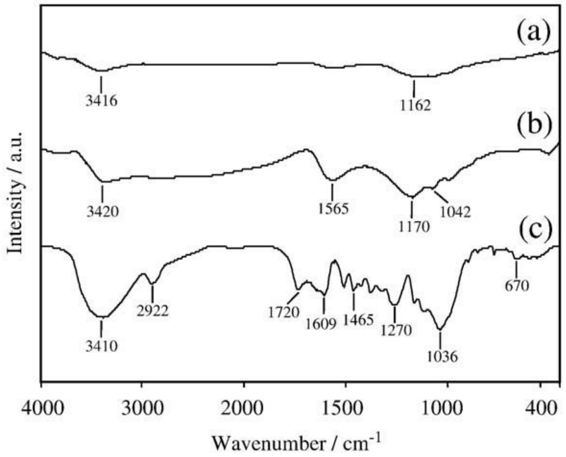


**Fig. 3.** FTIR spectrum of: (a) AC-700, (b) AC-500 and (c) Oil Palm Shell.

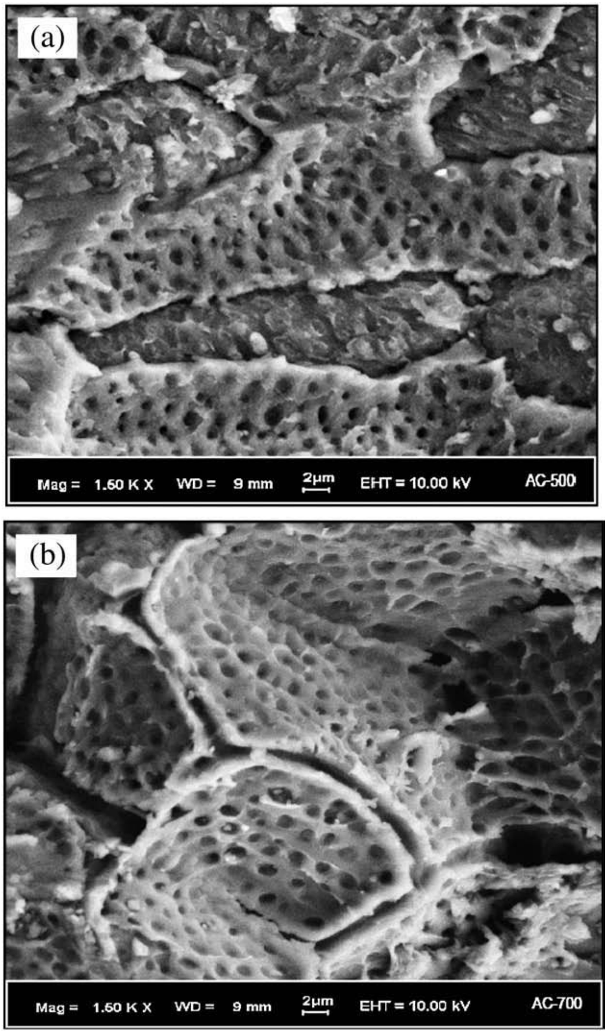


**Fig. 4.** FESEM micrographs of: (a) AC-500 and (b) AC-700.

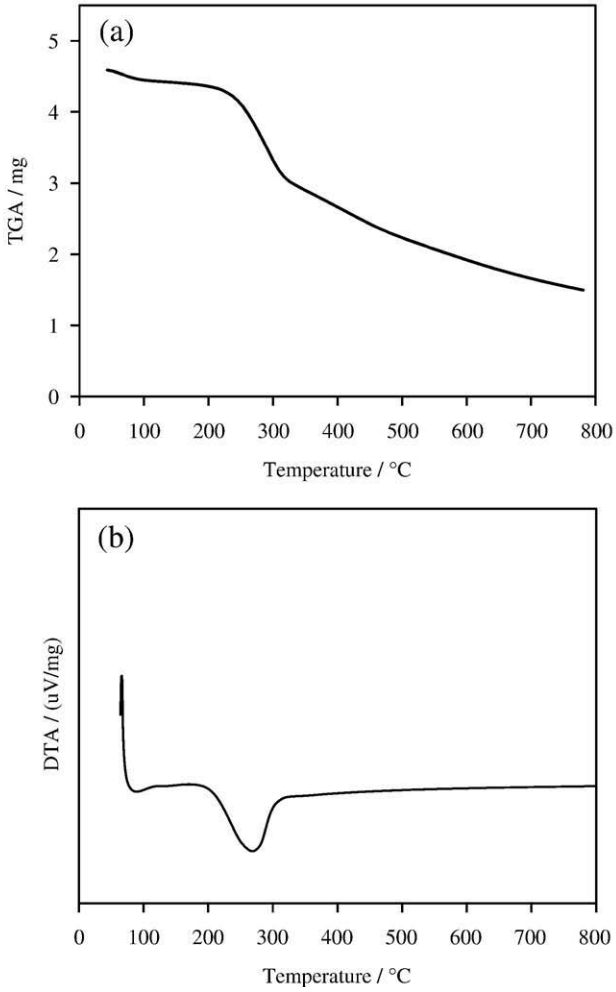


**Fig. 5.** Thermal stability of oil palm shell treated with $H_3PO_4$ from: (a) TGA and (b) DTA.

including 1:1, 2:1, 3:1 and 4:1. Results indicated that the lowest hydrogen peroxide concentration ($H_2O_2$: sulfur = 1:1) has the lowest efficiency to eliminate sulfur. This was because based on the ratio, the $H_2O_2$ concentration ($H_2O_2$: sulfur ~1: 1) was lower than the stoichiometric ratio ($H_2O_2$: sulfur ~2: 1) as shown in Scheme 1. Thus, there was a limited amount of oxidant that can caused incomplete conversion of sulfur compounds to sulfone. On the other hand, when working with excess of $H_2O_2$ ($H_2O_2$: sulfur >2:1), the reaction rate was higher. Based on the result, oxidation with a ratio of $H_2O_2$: sulfur = 3:1 showed the optimum sulfur removal but it exceeded the stoichiometric ratio. This was because in diesel, besides sulfur-containing compounds, nitrogen-containing compounds and aromatic condensed ring hydrocarbons were also present. Thus, the competition between these compounds for the oxidant will leads to higher consumption of the oxidant than expected. So, oxidation was enhanced when higher concentration of oxidant was used.

In this study, the hydrogen peroxide was reacting according to three reaction pathways, two oxidation pathways and a decomposition pathway as shown in Scheme 1. Both oxidation pathways proceeds via radicals attack on sulfur compounds to form their corresponding sulfones. In Pathway 1, the peroxyacetic acid was generated from mixing hydrogen peroxide and acetic acid as shown in Step 1 [38]. The decomposition of peroxyacetic acid catalyzed by activated carbon in Step 2 generates $^{\bullet}$OOH free radical which was a strong and the main oxidant for the oxidation of sulfur compounds. Peroxyacetic acid was a more effective oxidant than hydrogen peroxide due to the presence of a dissymmetry O–O bond with strong polarization in peroxyacetic acid which caused it to dissociate more readily than the symmetrical hydrogen peroxide in the presence of a reductant [39]. Meanwhile, some hydrogen peroxide which was not converted to peroxyacetic acid reacted according to Pathway 2. As reported by Oliveira et al. [40], the reaction was initiated by transferring an electron from the reducing site of the activated carbon to hydrogen peroxide to form a $^{\bullet}$OH radical, followed by the oxidation

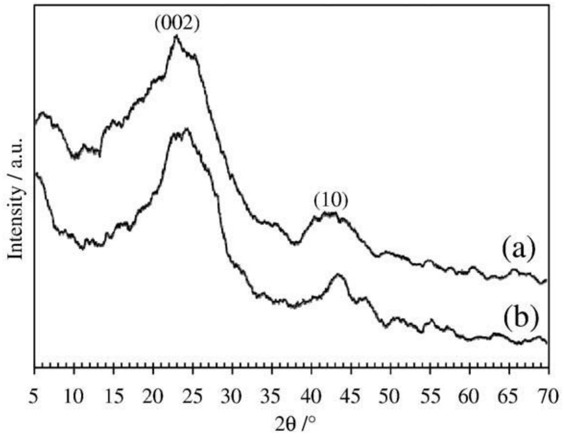


**Fig. 6.** X-ray diffractogram patterns of: (a) AC-500, and (b) AC-700.

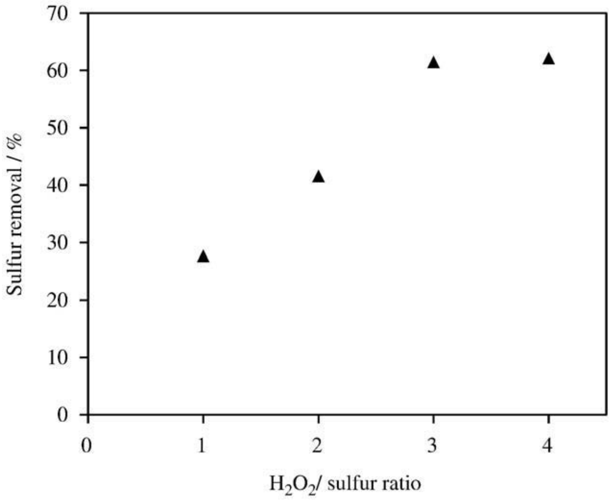


**Fig. 7.** The influence of different $H_2O_2$/ Sulfur Molar Ratios on Cat-ODS.

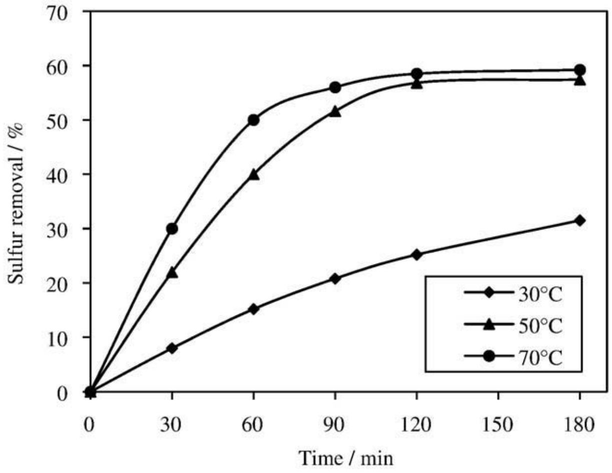
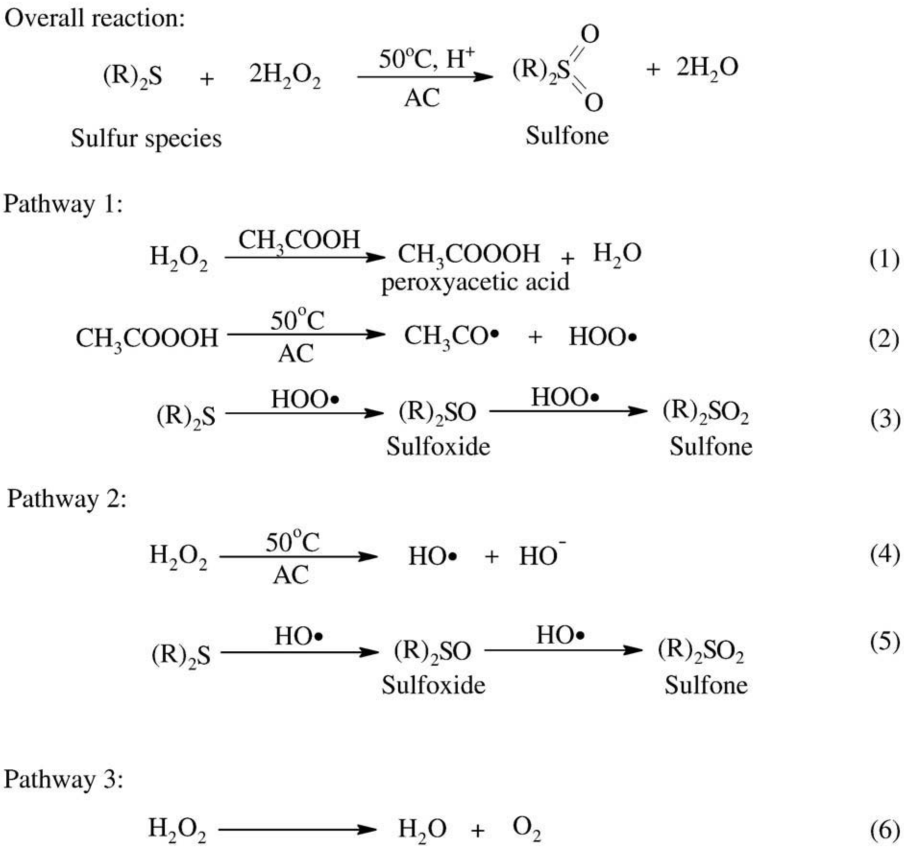


**Fig. 8.** The influence of temperatures on Cat-ODS.

of sulfur compounds. On the other hand, the oxidative activity of hydrogen peroxide in Cat-ODS process was inhibited and influenced by a competitive pathway which involved the decomposition of hydrogen peroxide to oxygen and water as shown in Pathway 3. A study conducted by Borah et al. [39] indicated that not all hydrogen peroxide introduced was utilized in situ formation of peroxyacetic acid and the remaining portion was decomposed with the evolution of oxygen gas.

Fig. 8 shows the efficiency of desulfurization in the Cat-ODS reaction versus the reaction time at three different temperatures (30 °C, 50 °C and 70 °C). An increase in the reaction temperature from 30 °C to 70 °C led to a remarkable increase in the reaction rate. However, oxidation at higher temperature was unfavorable due to the decomposition of hydrogen peroxide to undesirable side products other than hydroxyl radicals which decreases the efficiency of desulfurization process and affects the quality of diesel fuel. Besides that, reaction at temperature higher than 70 °C may lead to the oxidation of useful components in the fuel [41]. In view of these results, the reaction temperature employed for Cat-ODS was set at 50 °C. A longer reaction duration for oxidative desulfurization, will yield more complete oxidation of organosulfur compounds to their corresponding sulfones.

Fig. 9 shows the effect of different extraction solvents on the diesel fuel with and without oxidation process. Two types of extraction solvents were used namely acetonitrile and water–methanol (water:



Overall reaction:

$$(R)_2S + 2H_2O_2 \xrightarrow[AC]{50^\circ C,\ H^+} (R)_2S(=O)_2 + 2H_2O$$

Sulfur species → Sulfone

Pathway 1:

$$H_2O_2 \xrightarrow{CH_3COOH} \underset{\text{peroxyacetic acid}}{CH_3COOOH} + H_2O \quad (1)$$

$$CH_3COOOH \xrightarrow[AC]{50^\circ C} CH_3CO\bullet + HOO\bullet \quad (2)$$

$$(R)_2S \xrightarrow{HOO\bullet} \underset{\text{Sulfoxide}}{(R)_2SO} \xrightarrow{HOO\bullet} \underset{\text{Sulfone}}{(R)_2SO_2} \quad (3)$$

Pathway 2:

$$H_2O_2 \xrightarrow[AC]{50^\circ C} HO\bullet + HO^- \quad (4)$$

$$(R)_2S \xrightarrow{HO\bullet} \underset{\text{Sulfoxide}}{(R)_2SO} \xrightarrow{HO\bullet} \underset{\text{Sulfone}}{(R)_2SO_2} \quad (5)$$

Pathway 3:

$$H_2O_2 \longrightarrow H_2O + O_2 \quad (6)$$

**Scheme 1.** Cat-ODS reaction between oxidant and sulfur compound.

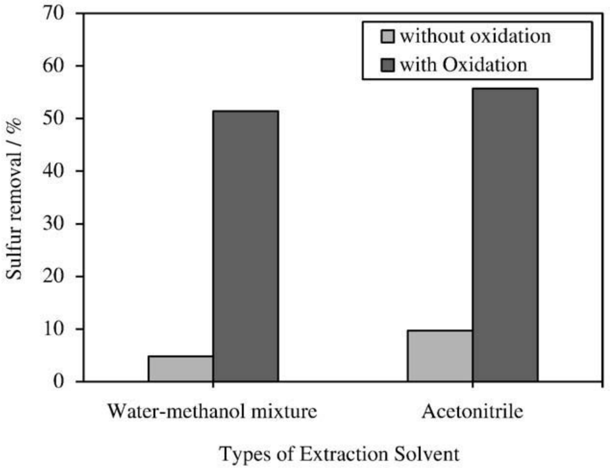


**Fig. 9.** The influence of extraction solvents on Cat-ODS.

methanol = 1:1 volume ratio) mixture. In this section, the dosage of the solvent with solvent: diesel volume ratio of 5:1 was used in extraction process. Generally, extraction with solvent: diesel volume ratio of 1:1 was normally found in other research works [42–45]. Extraction efficiency was increased with the volume of the solvent used. However, as reported by Ali et al. [41], the diesel loss increases with increasing dosage of acetonitrile and causing the yield loss problem. So, the extraction process with the combination of small dosage of solvent and with multiple extraction cycles can minimize this issue and was applied in this study. The conversion of sulfur compounds over granular functionalized-activated carbon catalyst decreases in the order: acetonitrile > water–methanol mixture. Direct extraction without oxidation resulted in less sulfur removal. This is probably due to the low polarity of sulfur compounds which lowers its affinity towards polar solvents and thus remained in diesel phase. Meanwhile, extraction after oxidation showed better results. This is because the sulfur compounds were oxidized into their corresponding sulfones and sulfoxides which have higher polarity and higher affinity towards polar solvent. In the case of water–methanol mixture, 50% of sulfur removal was achieved after oxidation while only 5% of sulfur removal was observed after extraction without oxidation. A similar trend was observed for acetonitrile; 58% of desulfurization with oxidation but only 10% of desulfurization was achieved in extraction without oxidation and similar result was reported by Ali et al. [41]. Besides that, the researcher found out that the maximum extraction efficiency with approximately 45% of sulfur removal can be achieved after double extraction with acetonitrile: diesel volume ratio of 1:1. Acetonitrile exhibits higher extraction activity because the primary oxidation product is sulfones which are highly polarized and hydrophobic compounds [46] and have low solubility in both organic diesel phase and aqueous phase but can easily dissolve in acetonitrile. Acetonitrile with lower surface tension facilitates the transfer of reagents between organic diesel layer and aqueous layer which leads to higher oxidation rate [47]. Moreover, although methanol has sufficient polarity, its density is 0.79 g/mL which is about the same as that of a typical light diesel oil which resulted in incomplete phase separation between hydrophobic and hydrophilic layers.

The prepared functionalized-activated carbon acts both as catalyst and adsorbent in this Cat-ODS process. Activated carbon provides the adsorption surface for the sulfur compounds and oxidation reaction to take place. It catalyzes the decomposition of $H_2O_2$ to $^{\bullet}OH$ or $^{\bullet}OOH$ free radicals which are powerful oxidant for oxidation of sulfur compounds to their corresponding sulfones. Results obtained showed that the sulfur oxidation without catalyst gave only 16.2% of sulfur removal in the presence of acetonitrile, glacial acetic acid and hydrogen peroxide including extraction of sulfur compounds by acetonitrile. This result was in agreement with a study conducted by García-Gutiérrez et al. [43], who reported that 16.8% of sulfur elimination was achieved in the reaction without the presence of catalyst.

**Table 2**
The effect of repetition oxidation in Cat-ODS.

| Catalyst[a] | $S_{BET}/m^2\ g^{-1}$ | Sulfur removal (%) | | |
|---|---|---|---|---|
| | | Single oxidation | Double oxidation | Triple oxidation |
| AC-500 | 489 | 57.4 | 79.9 | 91.3 |
| AC-700 | 560 | 59.9 | 77.5 | 88.2 |

[a] Sulfur removal without catalyst was 16.2%.

The oxidative activity of the synthesized functionalized-activated carbon catalysts was evaluated in the oxidative desulfurization of diesel. Table 2 shows the catalytic activities of different types of functionalized activated carbon on desulfurization of diesel. The results from Table 2 showed that the desulfurization efficiency in the reaction system without AC-500 or only in the presence of hydrogen peroxide and acetic acid was much lower than the system containing AC-500, hydrogen peroxide and acetic acid. This indicated that the presence of AC-500 can significantly improves the efficiency of the hydrogen peroxide–acetic acid system with an increment of 41.2%. The sulfur removal was increased from 16.2% in the system without catalyst to 57.4% in the AC-500–hydrogen peroxide–acetic acid system. A similar result was obtained by Yu et al. [1], who found out that the activated carbon was not only a good catalyst, but also a good adsorbent which resulted in much higher sulfur removal compared to the reaction system without activated carbon. According to them, another advantage of the activated carbon-catalyzed system was that it does not require high concentration of organic acid. Fig. 10 showed the dosage of AC-500 loading into Cat-ODS process. The results obtained revealed that the optimum dosage of catalyst was 10 g/L of diesel. Thus, in this Cat-ODS process, 0.5 g of the activated carbon was required to catalyze the oxidative desulfurization of 50 mL of diesel.

The adsorption properties of AC-500 and AC-700 were shown in Fig. 11. Both activated carbons showed low sulfur removal after 3 h adsorption of diesel fuel containing 2189 ppm of sulfur. Only less than 5% of sulfur removal was achieved after 3 h of adsorption. This result was less significant if compared to 91.3% of desulfurization in catalytic oxidative desulfurization process. This was because adsorption was a slow and time consuming process which can normally take 10 to more than 50 h for equilibrium adsorption depending on the physical and chemical properties of the adsorbate and the adsorbent. The properties such as the molecular size, pore size, functional groups and the surface functional groups were responsible for the interaction

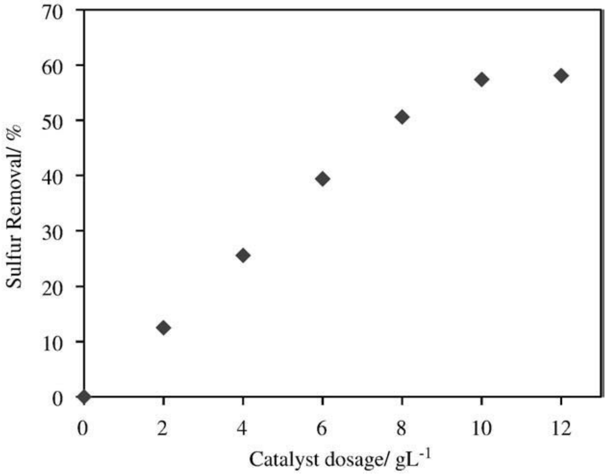


**Fig. 10.** The dosage of AC-500 loading into Cat-ODS.

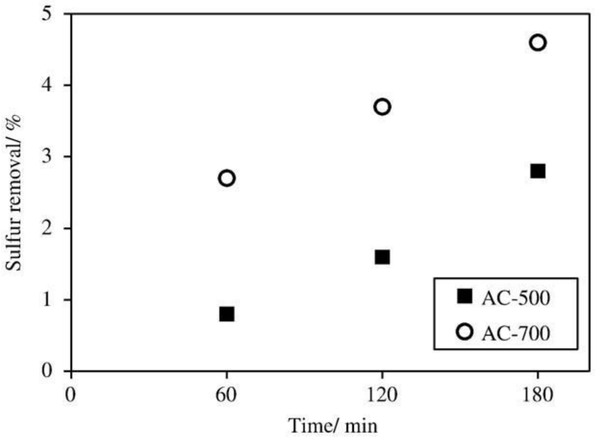


**Fig. 11.** The adsorption property of the activated carbon on sulfur removal in commercial diesel.

between the adsorbate and adsorbent. The gas chromatograph for the adsorption property of AC-500 was shown in Fig. 12(b).

The effect of the repeated oxidation step (single oxidation, double oxidation and triple oxidation) on the desulfurization of diesel fuel was also investigated. Table 2 shows that multiple oxidation cycles have a strong influence on the desulfurization process. After three oxidation cycles, the desulfurization efficiency increases remarkably with 91.3% of total sulfur removal. Results obtained from double and triple oxidation revealed that the catalytic activity of functionalized activated carbon was slightly decreased when the surface area was increased. Interestingly, AC-700 showed higher sulfur removal in single oxidation but with lower desulfurization efficiency when comes to double and triple oxidation. This phenomenon was most probably due to its larger surface area which aid in the adsorption of sulfur compounds. However, the adsorption of sulfur compounds on AC-700 causes the decrease of surface area, thus lowering its catalytic activity for both double and triple oxidation cycles. Besides that, the lower catalytic performance of AC-700 was probably due to less surface functional groups which were responsible for the catalytic action.

In contrast, AC-500 with lower surface area provided less adsorption of sulfur compounds which resulted in higher sulfur removal by catalytic oxidative process. Furthermore, the presence of various surface functional groups especially the acidic groups such as the C O, P O and P OOH groups as shown in FTIR spectrum will assist in the catalytic activity of the activated carbon. According to Yu et al. [1], the oxygen-containing functional groups especially the carbonyl group has a close relationship with the adsorptive and catalytic properties of the activated carbon. They reported that the acidic groups were electron withdrawing groups or electron acceptors while the sulfur atom in the sulfur compounds were electron donor. The interaction between them will lead to the formation of donor–acceptor complexes on the carbon surface. In other words, these acidic functional groups have strong affinity towards the sulfur compounds which caused the sulfur species to be initially physisorbed and then chemisorbed on the carbon surface. Once the sulfur compounds were chemisorbed, it formed active species on the carbon surface

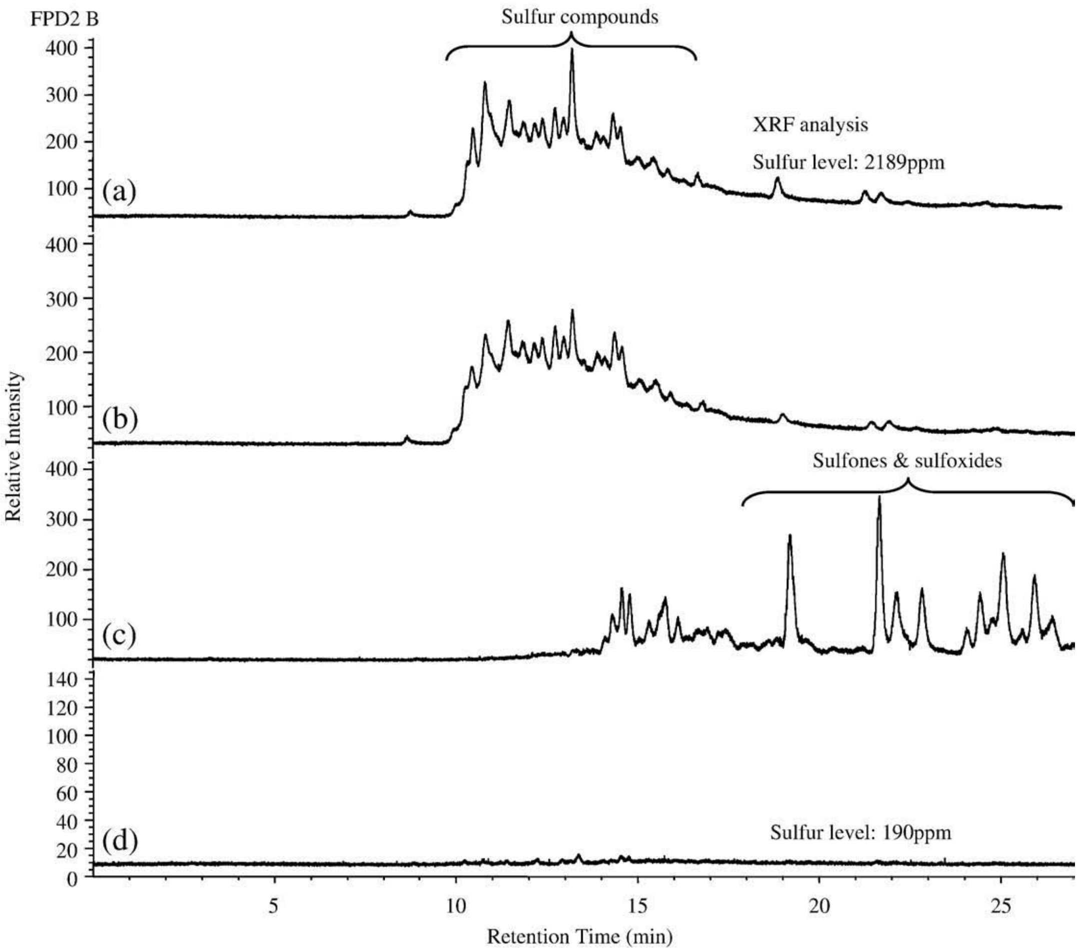


**Fig. 12.** GC-FPD chromatograms of (a) original Malaysian diesel, (b) After 3 h adsorption by AC-500 without oxidation, (c) treated diesel before extraction, and (d) treated diesel after extraction (note: the scales are different).

which were less stable and more readily oxidized by nearby oxidant. Fig. 12 showed the GC-FPD chromatograms of original and treated Malaysian diesel. These chromatograms suggest that most sulfur compounds present in the diesel were oxidized and removed during solvent extraction.

## 4. Conclusion

$H_3PO_4$ is a suitable activating agent for the preparation of high porosity carbons with high proportion of microporosity from oil palm shell. Granular functionalized activated carbon exhibited high catalytic activity in Cat-ODS with $H_2O_2$ as oxidant. The catalytic activity of the functionalized activated carbon does not depend on its specific surface area. Higher hydrogen peroxide concentration yield more complete oxidation at higher oxidation rate. Acetonitrile was used as the extraction solvent instead of the water–methanol mixture due to the higher solubility of sulfone in acetonitrile. Multiple oxidation cycles can improve the reaction efficiency in Cat-ODS reaction. After the catalytic oxidative treatment, commercial diesel fuel containing 2189 ppm sulfur was successfully reduced to 190 ppm of sulfur by using the hydrogen peroxide-granular functionalized activated carbon–acetic acid system (91.3% of total sulfur removal). These results may indicate that granular functionalized-activated carbon has the potential to be used as catalyst in Cat-ODS to meet the future regulation of sulfur in diesel fuels.

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