Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

Efficient Photo-Catalytic Desulfurization of Real Diesel Fuel Using Tungsten Oxide Decorated Porous Purslane-Derived Biochar for Clean Energy Generation and Environmental Remediation

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Abstract

A critical stage in the production of diesel fuels is the extreme reduction of sulfur compounds, which helps shield the environment from harmful emissions. It is also economically advantageous to use a process that is cost-effective for this type of work. In keeping with these ideas, this work presents the photocatalytic method of producing low-sulfur diesel fuel while being exposed to visible light. During this research plan, a fabricated structure consisting of tungsten oxide and porous purslane-derived biochar is presented as a new photocatalyst. Using hydrogen peroxide as an oxidant could result in notable improvements in the desulphurization degrees by the 10wt% WO_3/Biochar photocatalyst. Through the use of X-ray diffraction, Fourier-Transform Infrared spectroscopy, N2 Adsorption -Desorption, Energy Dispersive X-ray, and scanning electron microscopy, the physical properties of the prepared catalyst were studied, and photoluminescence was used to assess its photo properties. To achieve 97.19% desulfurization efficiency, the reaction time, oxidant amount, and catalyst dose were investigated. The desulfurization efficiency can reach 97.05% after five cycles.

Keywords: Photo-catalysis, Desulfurization, Tungsten oxide, porous purslane biochar, real diesel fuel.

1. Introduction

Air pollution exposure is considered the greatest risk factor for environmental health, according to the World Health Organization (WHO). One of the sustainable goals of the world is reducing greenhouse gas emissions. In order to achieve this, nations have concentrated their efforts on enforcing stringent laws, encouraging sophisticated transit systems and inventive building techniques, and making investments in cleaner energy derived from fossil fuels by capturing, storing, and sequestering greenhouse gases. The two ways that the sulfur content of fuels is related to increased air pollution are the direct emissions of harmful sulfur oxide (SO_x) compounds into the atmosphere, which cause acid rain, and the indirect deactivation/poisoning of catalysts used in refining systems and reduction in the effectiveness of emission control devices[1], [2].

Therefore, during the past few decades, research and development of efficient methods for reducing sulfur compounds in fuel oil has garnered special attention, as well as the implementation of strict environmental rules on the sulfur content of fuels. Many forms of inorganic sulfides, disulfides, and mercaptans have been successfully managed through the application of the traditional hydro-desulfurization (HDS) process. But due of a number of intrinsic drawbacks, including harsh operational conditions and increased energy waste, this technology is unable to satisfy the necessities for the deep desulfurization of fuels. Specifically, it is inefficient at eliminating aromatic sulfur compounds[3], [4].

Instead of using HDS for deep desulfurization of diesel fuel fractions, Oxidative desulfurization (ODS) has been proposed as a viable substitute method. Low temperatures and atmospheric pressure triggers a chemical reaction between sulfur compounds and an oxidant in ODS, H_2O_2 is commonly used as an oxidizing agent owing to its environmentally friendly reaction product (H_2O). In this kind of procedure, the sulfur compounds are usually converted into sulfur oxides, which make it easier to remove them later on with a solvent extraction stage. Because of the high time and cost requirements as well as the possibly dangerous emissions resulting from the use of organic solvents, this technology may not be widely used [5], [6].

As a result, it is anticipated that these restrictions on the desulfurization of sulfur compounds would promote the creation of more innovative and viable methods for producing environmentally ecofriendly liquid petroleum. Various techniques, including extraction using ionic liquids[7], [8] , selective adsorption [9], photocatalytic desulfurization[10], oxidative desulfurization (ODS)[11], biodesulfurization, solvent extraction[12], [13], microwave-assisted extraction[14], [15] and other processes , have been established to date to remove refractory sulfur species from diesel fuels[16].

In recent times, photocatalysis has emerged as a proficient technique for eliminating sulfur compounds from diesel fuel fractions or their surrogate molecules. This method involves the desulfurization of sulfur compounds with a catalyst and through a light irradiation source. This process may be one of the innovative, cost-effective techniques used as a new,

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Receive Date: 17 October 2024, **Revise Date:** 16 November 2024. **Accept Date:** 21 November 2024
DOI: https://doi.org/10.21608/ejchem.2024.328397.10630

alternative trend for the elimination of sulfur[17]. This method was still required to report on comparatively little amounts of sulfur compound elimination, though. In general, the offered photocatalysts in such a procedure are relevant to these desulfurization level constraints. Typically, these photocatalysts were composed of individual transition metal oxides or supported on carbonaceous structures or non-transition metal oxides[18]. To obtain higher degrees of desulfurization, it is therefore imperative to introduce improved photocatalysts with increased optical characteristics that offer high attack performance towards sulfur compounds and high adsorption capacity. Numerous photocatalysts, including zinc oxide, tungsten oxide, and titanium oxide, have been developed for the photocatalytic oxidative desulfurization of pollutants containing organic sulfur. WO3 is a robust and promising catalyst to address these environmental problems because to its stability, non-toxicity, resistance to photocorrosion, and great oxidation capability of photo generated hole [19], [20]. Modification of the particle size improvement of the morphology, and crystal structure are ways to increase the photocatalytic activity of WO_3[21]–[23].

The removal process is designated to be done using waste generated bio-carbon modified with metals oxides sites. As a potentially useful substance for environmental remediation, biochar is created by pyrolyzing biomass from carbon-rich sources (such as agricultural wastes) in an oxygen-limited environment [24]. Among its extraordinary physicochemical characteristics are a specific surface area, a large number of active functional groups on the surface, and a porous structure. Apart from its exceptional adsorption ability, biochar can also take up electrons and take part in electron transport. In addition, biochar's great stability makes it a great support material for photocatalysts[25], [26].

Since they are entirely natural, abundant, sustainable waste with functionalization, antioxidant, and antibacterial qualities, natural plant and agricultural wastes have found widespread application in a variety of industrial fields. In nature, Portulaca oleracea L. is one such plant-based substance that is widely available. This is a herbaceous annual plant that thrives in warm areas and is a member of the Portulacaceae family. As an antipyretic, an antiseptic, and other properties, purslane has been utilized as a traditional treatment in numerous nations. Portulaca oleracea L. was the primary raw material for the preparation of biochar in this investigation[27], [28].

The study's main objective is to combine a carbon-rich material (bio char) with suitable semiconductors that are affordable, efficient in visible light, and have good charge separation. The semiconductors used are WO_3, which is one of the most widely used semiconductors or photocatalysts due to its higher photocatalytic capacity, high stability, low cost, and lack of toxicity. The ultrasound assistance impregnation technique was used to synthesis of 10wt. %WO_3/biochar composite. A low-sulfur diesel fuel was produced by utilization of the produced WO_3/biochar composite.

2. Experimental

Materials:

Ammonium paratungestate $[(NH_4)10(H_2W_{12}O_{42})\ .4H_2O]$, hydrogen peroxide ($H_2O_2$) and absolute ethanol from sigma Aldrich. The diesel fuel fraction (boiling range 175-340 °C) used in this work which was kindly supplied by the Suez oil petroleum company.

2.1. Preparation of Biochar

The Portulaca oleracea plant; whole plant ;was collected, washed and dried at 60 °C overnight. After drying the whole plant; it was pyrolyzed in presence of nitrogen at 600° C. for 6h.

2.2. Preparation of catalyst

Ammonium paratungestate $[(NH_4)10(H_2W_{12}O_{42})\ .4H_2O]$; tungsten precursor was calcined in a muffle in presence of oxygen at 500 oC for 4h to produce WO_3. Then the 10% WO_3 / biochar composite was prepared according to the pre-pyrolysis technique as follows: 10 gm of prepared biochar in 20 ml of an absolute ethanol was ultrasonicated for 30 min. after that the appropriate amount of tungsten oxide in suitable amount of ethanol was added drop wise to the biochar under effect of ultrasound oscillation for 2 h. The ultrasonic vibration was afterward stopped, the composite was then filtrated and washed several times with deionized water,, and the obtained catalyst was then dried in the oven at 60° C overnight.

2.3. Photocatalytic reaction

The photo catalytic oxidative desulfurization of real diesel oil (Sulfur content= 890 ppm) was carried out under constant stirring of round flask contain 25 ml of feed, 3ml H2O2 (as oxidant) and 1 gm of prepared catalyst (10 wt.% WO_3 /Biochar), the mixture was stirred for 30 min before irradiation to reach the adsorption-desorption equilibrium state. Then we use 500 watt linear halogen lamp (visible irradiation with a wavelength of 550 nm). We studied several factors as; time (min), volume of oxidant (ml), and dose of catalyst (gm) to reach the optimum conditions for oxidative the sulfur compound. For recycling the used catalyst was collected, washed and dried at 80 °C, then used with fresh oxidant and fresh feed with certain amount and for certain time.

2.4. Characterization

Using an XRD instrument (Germany) version X'Pert Pro equipped with Ni-filtered Cu-K radiation (λ = 0.1542-nm), X-ray diffraction (XRD) patterns were identified. Using a Bruker Tensor 27 infrared spectrometer (Germany), Fourier transforms infrared (FTIR) analysis was recorded. The samples' surface morphology was photographed using a Zeiss ULTRA Plus scanning electron microscope (SEM), which was outfitted with an EDS (dispersive X-ray spectrometer) (Germany). Using a spectrofluorometer (JASCO FP-6500, Jasco International CO., Ltd., Tokyo, Japan) with an excitation wavelength set at l ¼ 300 nm, the photoluminescence characteristics were measured at room temperature. Using Quantachrome Nova 3200 instrument (USA) for N2 adsorption–desorption isotherm.

3. Results and discussion

3.1.XRD

Fig. 1 presents the XRD pattern of biochar, WO_3 and WO_3/biochar. As we show in biochar pattern there is a broad diffraction peaks at $2\theta = 15–30^{\circ}$ which is attributed to C (002), that indicates the amorphous carbon structures which containing randomly oriented aromatic carbon sheets [29]. Also there is a sharp peak at $2\theta = 28^{\circ}$ which indicated to the carbonated mineral [28]. The highly crystalline WO_3 shows sharp and intensive peaks at $2\theta = 15^{\circ}$, 25°, 26°, 29°, 30°, 35°[30], [31]. The pattern of WO_3/biochar indicates small peaks at $2\theta = 29^{\circ}$ and 30° for WO_3. And also, there is a peak at $2\theta = 28^{\circ}$ for the carbonated mineral.

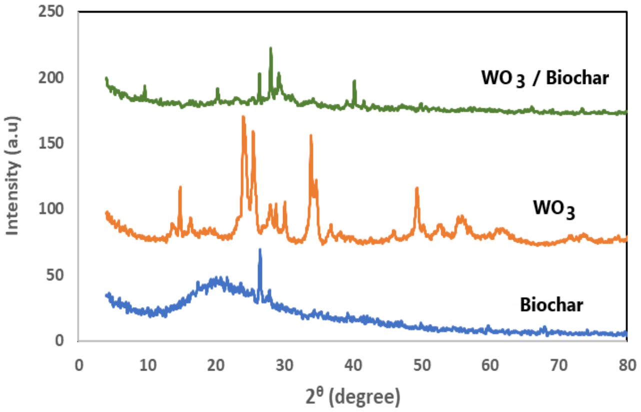

Fig. (1): XRD of the prepared biochar, WO3 & WO3/biochar

3.2. SEM

The morphology of the prepared biochar from Portulaca oleracea plant presented by the scanning electron microscope figure (2-a); as we show the structure has many cavities that increase the activity of the prepared materials. There are some crystallites formed above the surface of biochar figure (2-b) which indicates the formation of WO_3 on the surface of biochar and that matches with XRD pattern figure (1).

According to the elemental mapping (EDS) for WO_3/biochar sample figure (3), the percent of elemental composition was; 62% C, 25% O and 13%W.

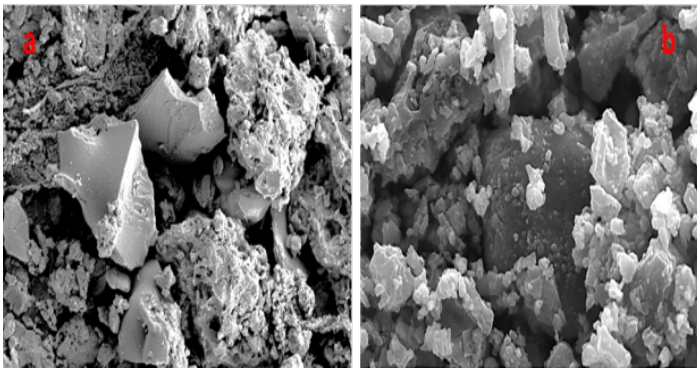

Fig.(2): Scanning electron microscope of (a)biochar (b)WO3/ biochar

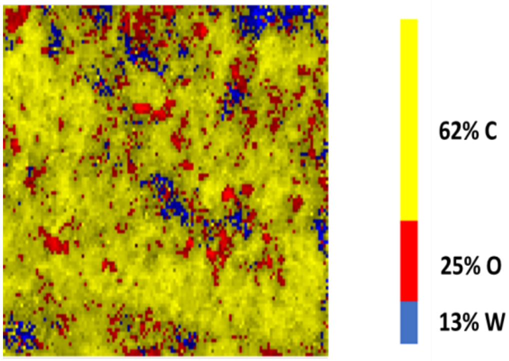

Fig. (3): Elemental mapping (EDS) of WO3/biochar

3.3. Photoluminescence (PL)

The prepared biochar and WO_3/biochar were excited by wavelength $\lambda = 300$ nm to examined the photo properties of them. As we shown in figure (4) there is a luminescence peak appears at $\lambda = 498$ nm for biochar and WO_3/biochar. But the intensity of the peak in case of biochar is higher than WO_3/biochar; that indicates the electrons in the valence band in case of WO_3/biochar move slowly to the conduction band and cause strong recombination between excited electrons and holes, that explain the incorporation of WO_3 with biochar increase the photo-activity of the catalyst. Prior to being stabilized by photo-emission, the valence band electrons first migrate to the conduction band. Because excited electrons recombine quickly, the PL intensity rises as the number of released electrons grows and holes which consequently lowers the catalyst's photoactivity. There is a direct correlation between the energy and emission wavelength. Band-gap brought on by a photo-generated hole recombining with the oxygen vacancy is occupied by an electron.

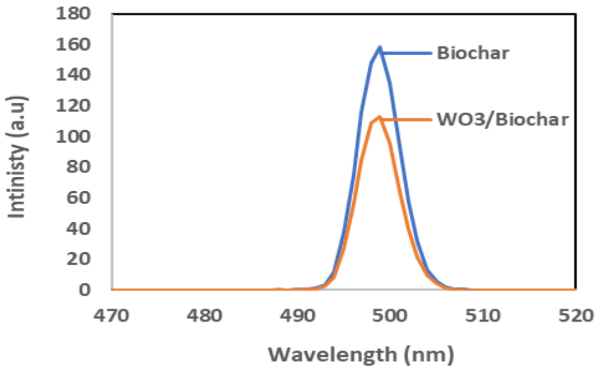

Fig.(4): photo luminance of biochar and WO3/biochar

3.4. FT-IR

As we shown in FTIR pattern for biochar sample figure (5) there is a beak at 1583 cm^{-1} which is indicating for C=C and other at 1441 cm^{-1} indicates the presence of carbonate species. Incorporation of WO_3 on biochar appears beak at 866 cm^{-1} due to the stretching vibration of W=O and W-OH appears at 1070 cm^{-1}.

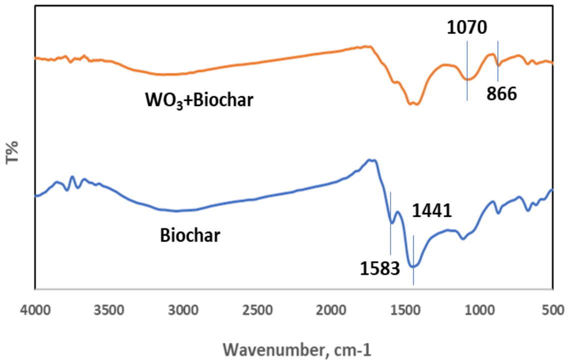

Fig.(5): FTIR spectrum of Biochar and WO3/Biochar

3.5. N2 Adsorption -Desorption

By studying N2 adsorption-desorption for the prepared samples figure (6), we noticed that the biochar and WO_3/biochar gives type IV isotherm, that type appears when capillary condensation takes place. At pressures lower than the gas's saturation pressure, gases condense in the solid's microscopic capillary pores. It displays the production of a monolayer at lower pressures, followed by the formation of multilayers. Due to the difference between desorption isotherm, which occurs when the partial pressure is reduced, and the adsorption isotherm, which occurs when the partial pressure is raised, the hysteresis loop was appeared. Biochar indicates H4 hysteresis loop which appears in case of narrow pores, while H3 hysteresis loop of open-ended pores presented in WO_3/biochar As we shown in table (1) the surface area decreased from 150 m^2/g to 100 m^2/g when loaded the WO_3 on biochar surface, but the pore volume increased from 0.2 cc/g to 0.68 cc/g that indicates the particles of WO_3 creates pores with larger size and larger pore volume than that present in biochar.

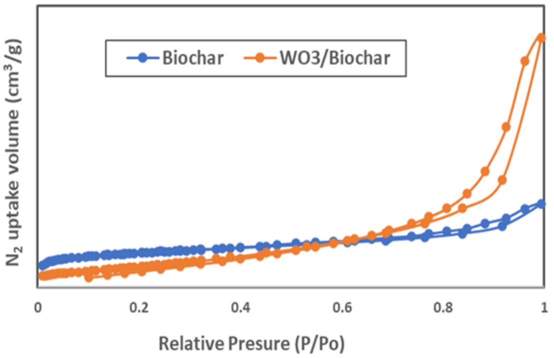

Fig. (6): Nitrogen adsorption–desorption isotherm for Biochar and WO_3/Biochar

Table (1): The physico-chemical characteristics of the Biochar and WO_3/Biochar

Sample	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore size (nm)
Biochar	150	0.2	1.5
WO_3/Biochar	100	0.68	3

3.6. Photocatalytic activity in desulfurization process of real diesel fuel:

Prior to the photocatalytic experiments, the prepared photocatalysts' adsorption capacities towards sulfur compounds were investigated in the dark with conditions (time=60 min., at room temperature, catalyst dose= 3 gm and 10ml H_2O_2). Due to the porous structure of biochar the catalyst demonstrated an approximately 27% desulfurization efficiency with equilibrium in 30 minutes.

3.6.1. Effect of irradiation time:

At this step, the impact of varying the operating time on the desulfurization process's quality is examined. Figure 7 displays the gathered desulfurization efficiency percentages throughout a time span of 30 to 150 minutes, with a 30-minute interval between time increases. By extending the process duration to achieve the maximum at 90 minutes, the desulfurization efficiency was raised to achieve 77.53 %. By extending the operating durations, this discovery alludes to the enhanced interactions between the particles of the WO_3/biochar photocatalyst and the molecules of diesel fuel. A reduction of sulfur removal efficiency exploits is observed as 74.16% and 71.91% when increasing the reaction time to 120 and 150 min respectively. Covering the catalyst's surfaces in monolayers of adsorbed sulfur compounds could provide an explanation for this observation. This surface covering may therefore restrict the photocatalytic activities that the catalysts being used are able to accomplish. In addition, extending the time allows the conversion of H_2O_2 to H_2O by recombination of the excited OH· radicals of hydrogen peroxide, which negatively affects the efficiency of the desulfurization process. Therefore, it was discovered that using an operational time of 90 minutes was ideal for achieving successful desulfurization activities using the WO_3/biochar composite.

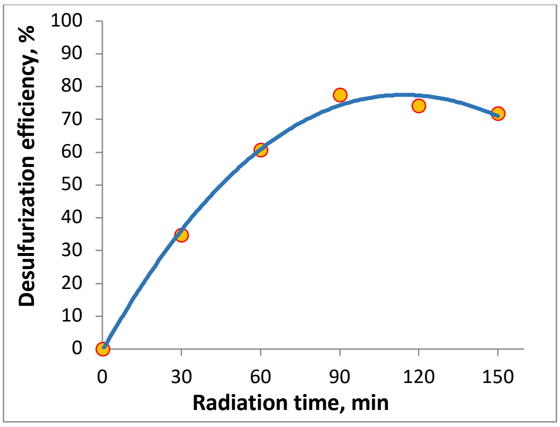

Fig.(7): Variation desulfurization efficiency of diesel fuel by the radiation time change.

3.6.2. Impact of oxidizing agent, H_2O_2 amount:

After the previous stage was completed, a 90-minute operating duration was determined to be the ideal setting for the current photocatalytic desulfurization investigation. Hydrogen peroxide (H_2O_2) produces extremely reactive hydroxyl radicals (OH•) that can oxidize organic sulfur species present in diesel fuel, creating sulfoxides and sulfones. This is utilized to boost desulfurization reactivity and prevent ODS processes from being hindered under the action of light radiation. Various H_2O_2 volumes (1, 3, 5, 7, 10, and 15 ml) were used in this investigation step.

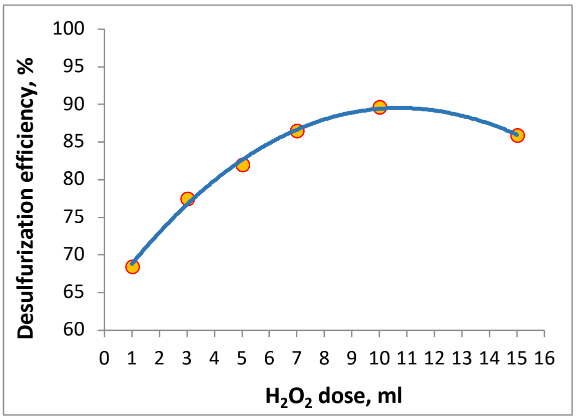

Fig.(8): Photocatalytic activity of WO_3/biochar composite under the influence of H_2O_2 dose.

Fig. 8 shows how the percentages of desulfurization efficiencies are affected by an increase in oxidizing agent doses. By increasing the hydrogen peroxide volume to 10 ml, the elimination of sulfur compounds was enhanced; as 89.66% desulfurization efficiency percentage. The observed increases in desulfurization efficiency are explained by a growth in OH radicals, which may raise the probability of oxidizing the sulfur compounds currently present in the diesel fuel component into sulfones. An easy extraction process might then be used to remove these oxidized compounds from the diesel fuel. The desulfurization efficiency (85.95%) may suffer if an excessive amount of oxidizing agent (15 mL) is used. Increasing the amount of H_2O_2 in the reaction vessel can account for the observed drop in desulfurization activity by increasing light absorption. That due to when H_2O_2 concentration raises increases the particles in the media and that inhibits the catalyst's active sites towards the desulfurization process. As a result, the catalysis particles may only be able to achieve a limited amount of photo-activity, which would reduce the removal of sulfur compounds.

3.6.3. Influence of catalysts dose

Further testing was done on the WO_3/biochar composite by investigate the effect of composite dose (0.1, 0.5, 1, 3,5, and 7 gm) on desulfurization efficiency of the diesel fuel enclosed 890 ppm sulfur content, in order to ascertain this cost-effective photocatalyst's possible applications in the production of clean energy and environmental restoration. As the photocatalyst dose in the processing media is increased to 3 gm, the percentage of desulfurization increases noticeably, as seen in figure 9. The observed increases in sulfur removal can be explained by an increase in photocatalytic sites on the WO_3/biochar photocatalyst, which occurs when the composite dosage is inflated. Next, a minor rise in the desulfurization percentage coincided with the increase in photocatalyst dosage from 3 to 5 gm in the operated media.

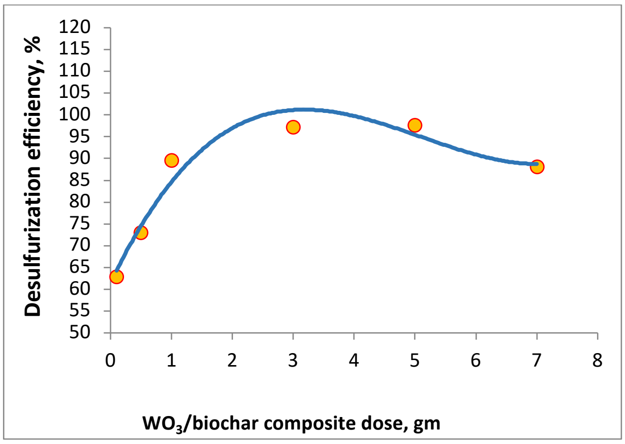

Fig.(9): Impact of WO_3/biochar photocatalyst dose on the photocatalytic desulfurization efficiency.

According to earlier reports, the reason for the slight rise in sulfur removal percentage is that light irradiation disperses among more particles than applying different doses of photocatalyst does. As a result, the introduced composite may achieve a less notable degree of photocatalytic performance, which could lead to a marginal increase in the percentage of sulfur elimination. We discovered that the effectiveness of the sulfur removal procedure decreased when we kept adding more catalyst to the operated media. This observation supports the previously provided explanation, which states that the removal process is hampered by an increase in catalyst dose because to light ray scattering. With consideration for the economic perspective and the results presented in Figure 9, the maximum percentage of sulfur removal was achieved with a catalyst concentration of 3 grams. This is because the 8 gm/L increase in catalyst dose each run does not correspond with the small increase in removal process efficiency from 97.19 to 97.75 % by 3 and 5gm WO3/biochar photocatalyste dose respectively. As a result, 3 grams was determined to be the ideal photocatalyst dose.

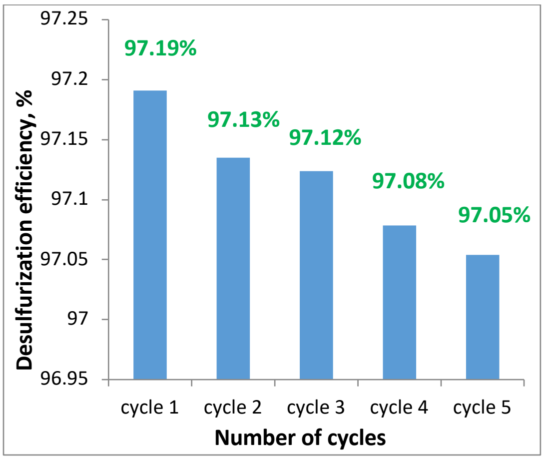

Fig. (10): Influence of recycle times of the WO_3/biochar composite on the photocatalytic desulfurization efficiency.

3.7. WO3/biochar Photocatalyst reusability

It was vital to investigate the prospect of reusing the added photocatalyst in order to increase the desulfurization process's viability and economic worth. At this point, a recycling procedure had been applied to the composite structure (WO_3/biochar photocatalyste), which displayed the highest degree of sulfur elimination. Firstly, the composite structure was repeatedly cleaned using an ethanol/deionized water mixture. Following the application of this combination, the sample was repeatedly cleaned with deionized water before being sent to an oven to dry at 60 °C. By that time, the WO_3/biochar photocatalyst had been recovered and was being used to desulfurize diesel fuel feedstock under ideal circumstances, as had been established in earlier portions. Over five cycles, the recovered photocatalyst displayed a nearly constant desulfurization efficiency percentage of 97.19% (fig. 10).

3.8. Mechanism of photo-desulfurization

We studied the effect of photo on dibenzothiophene (example for sulfur compound that already present in diesel fuel) figure (11). The hydrogen peroxide in presence of light converted to hydroxyl radical (oxidizing agent) and the oxygen in WO_3 converted from O_2 to $O_2^{\cdot-}$ radical, that radical catalyze the conversion of bivalent sulfur of dibenzothiophene to hexavalent one which presents in sulfone. The dibenzothiophene sulfone is more polar than dibenzothiophene and that facilities their removal by polar solvent.

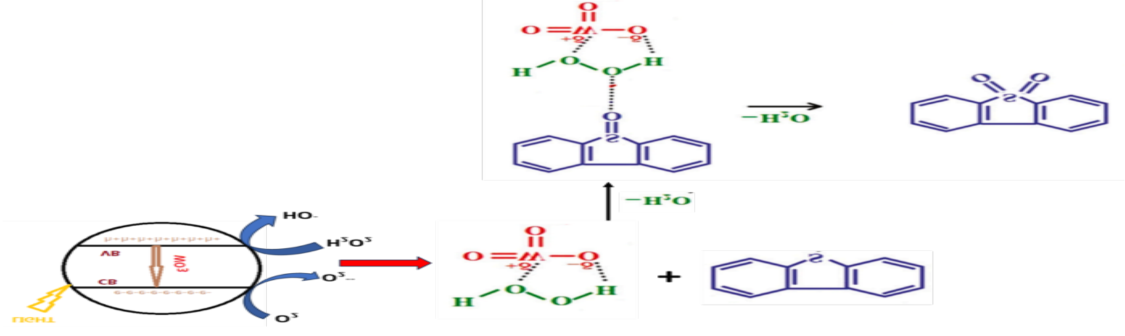

Fig. (11): A proposed mechanism of the sulfur compound removal photo-reaction process.

4. Conclusion

The 10 wt.% WO_3/biochar photocatalyst have been prepared as an economic photocatalyst using raw materials purslane plant for Porous purslane-derived biochar production and decorated with WO_3 by impregnation route. The structural characteristic of the prepared photocatalyst was proved by XRD, FT-IR and elemental mapping analysis. The surface morphology and the photo properties of the prepared WO_3/biochar composite were examined by scanning electron microscope and photoluminescence testes respectively. The WO_3/biochar photocatalyst was examined in photocatalytic desulfurization of a real diesel fuel (890 ppm S-content) and H_2O_2 as oxidant at different factors as irradiation time (30, 60, 90, 120 and 150 min), catalyst amount (0.1, 0.5, 1, 3,5, and 7 gm) and H_2O_2 amount (1, 3, 5, 7, 10, and 15 ml) under 500 watt linear halogen lamp (visible irradiation with a wavelength of 550 nm). We were reached to 97.19% desulfurization efficiency at 90 min irradiation time with 3 gm WO_3/biochar photocatalyst and 10 ml H_2O_2 as oxidant. Additionally, this composite shows a stable level of desulfurization over five cycles of reusability, which is highly reliable. Therefore, we can conclude that the WO3/biochar photocatalyst possessed highly stable activity and recyclability, supporting its innovative applications for improved environmental management.

Conflicts of interest

"There are no conflicts to declare"

Formatting of funding sources

No fund

Acknowledgments

Special thanks to the the Egyptian Petroleum Research Institute (EPRI), Cairo, Egypt. for providing facilities to realize the work.

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