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Characterization and kinetic studies of oxidation desulfurization of model diesel fuel in an oscillatory baffled reactor using co-magnetic active oxides over activated carbon catalyst

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Abstract

Oxidative desulfurization (ODS) has attracted interest in the academic and industrial fields to meet new, stringent environmental legislation and produce environmentally friendly fuel. In this work, catalytic oxidative desulfurization of dibenzothiophene (DBT) compounds in diesel fuel is studied using a co-magnetic active oxide over an activated carbon (Fe_2O_3 + MnO_2/AC) catalyst. DBT oxidation reactions are conducted in new oscillatory and non-oscillatory baffled reactors (OBR and NOBR). New central baffles for handling catalyst particles as a fixed bed in the OBR are developed for the first time. ODS process is examined using hydrogen peroxide as oxidant under different operating parameters: temperatures: 30 - 90 °C, oxidation times: 3–12 min, frequency: 0.5 - 2 Hz, and amplitude: 3 -12 mm. The results observed that the highest desulfurization efficiency (98.1 %) is achieved under the best conditions (90 °C, 12 min, 2 Hz, and 12 mm) in OBR. The dramatic DBT oxidation in a short desulfurization time is mainly attributed to the synergistic effect of oscillatory flow and the high activity of the synthesized catalyst. The desulfurization kinetic model is examined under the best conditions. Kinetic results show that ODS reactions follow a first-order model. Also, a low activation energy (3.68 kJ/mol) is determined, which proves rapid DBT oxidation at a lower required energy.

Keywords: DBT oxidation; Co-active catalyst; Activated carbon; Oscillatory baffled reactor; Kinetic parameters.

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1- Introduction

Diesel fuel is a complex mixture that primarily comprises hydrocarbons, as well as considerable amounts of organic sulfur molecules, especially thiophene and its derivatives such as dibenzothiophene, 4,6-methyldibenzothiophene, etc. [1, 2]. During combustion, diesel fuels release sulfur oxides, which have a severe negative impact on human health and the environment, increasing air pollution and acid rain [3-5]. Also, sulfur compounds caused serious industrial problems, including equipment corrosion and poisoning/deactivation of catalytic materials [6, 7]. Therefore, strict world legislation has been adopted to determine the allowable sulfur content in diesel fuel. Thus, the US Environmental Protection Agency (EPA) and European agencies have established permissible sulfur levels of less than 15 ppm and less than 10 ppm, respectively [8, 9].

As a result, reducing and controlling sulfur content in diesel fuel is of great interest in both industrial and academic fields. Hydrodesulfurization (HDS) is the conventional technology for removing sulfur compounds from liquid fuels using catalytic materials and explosive hydrogen gas under high temperatures and pressures [10-14]. Although it has been a well-established technology, it has become insufficient due to the rapid development towards more sustainable environmental conditions [15, 16]. Also, HDS is an emitted risk H_2S and non-efficient in producing ultra-clean sulfur diesel fuel, owing to it has low reactivity towards removing refractory organic sulfur compounds, especially dibenzothiophene, which has driven the research to develop more appropriate and deep desulfurization technologies, such as oxidative, adsorptive, extractive, electrochemical, and bio desulfurization techniques [17-20]. Oxidative desulfurization (ODS) has proved to be an alternative to the traditional hydrogenation method, operating under mild conditions in the presence of an efficient catalyst and oxidant, and in the absence of hydrogen gas [21, 22]. It's a promising technology due to its economic efficiency, ease of use, and high effectiveness in removing refractory organic sulfur, and it produces clean fuel that meets new environmental standards [10, 23].

During oxidative desulfurization reactions, sulfur compounds are oxidized in the presence of a suitable catalyst and oxidant into sulfoxides and sulfones. These oxidized compounds have high polarity, making them easily separated from petroleum fuel using techniques such as extraction and adsorption [24, 25]. The essential

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challenge of ODS is selecting appropriate catalysts, oxidants, and reactor designs. Different oxidants are used for sulfur oxidation, including hydrogen peroxide, peracetic acid, air, and oxygen. Hydrogen peroxide (H_2O_2) is established as a more effective oxidant due to its availability, strong oxidizing ability, and the formation of green by-products (water) [24, 26]. Selection of a suitable catalyst is a critical factor in the development of ODS, as it depends on catalytic reactivity, selectivity towards sulfur species, optimal physicochemical characteristics, and efficient regeneration [27, 28].

Among numerous catalytic materials, activated carbon (AC) is by far the most suitable due to its large surface area, abundance, and ease of production from low-cost sources such as agricultural and waste materials [29, 30]. Loading magnetic (iron) and manganese active oxides onto activated carbon surface supports provides remarkable contact between these active oxide sites and reactants, thus boosting the activity of catalytic oxidation reactions due to their high stability and reusability, while maintaining semi-fixed reactivity for the removal of sulfur molecules. Amer et al. examined the catalytic reactivity of (8% Mn_3O_4/AC) catalyst in oxidizing and removing sulfur compounds from gas oil using a digital baffle batch reactor (DBBR) at various temperatures, oxidative periods, and oxidant amounts. The experimental data demonstrated that 93.33% desulfurization efficacy occurred at 90 °C for 45 min with 5 ml H_2O_2 [31]. Jian Wang et al. investigated the activity of the Fe/AC catalyst during the oxidative desulfurization of benzothiophene (BT) from model diesel oil using hydrogen peroxide as the oxidant under moderate conditions.

They found that 95.66% of BT was oxidized and removed at 60 °C, 1 atm, 0.15 g catalyst, 18 molar ratio of oxidant/S, and an initial BT content of 700 ppm, employing acetonitrile as the solvent for the extraction step via double passes [32]. Reactor design plays an essential role in producing ultra-low-sulfur fuel through an efficient, deep, and fast oxidative desulfurization process [33, 34]. An oscillatory baffled reactor (OBR) is a novel configuration of an oscillatory reactor that provides efficient, uniform mixing through the interaction between oscillatory fluid flow and internal baffles [16, 33, 35, 36]. OBR offers many benefits over conventional reactor designs, such as significant enhancement in mass rate, efficient heat transfer and temperature distribution, creation of plug-flow conditions under laminar flow, and long reaction times for optimal process efficacy [16, 34, 35, 37].

Numerous baffle designs have been developed for various physical and chemical applications in OBR, including helical, central, orifice, multi-orifice, and integral baffle designs [35, 38, 39]. In the present work, an oscillatory baffled reactor with a newly developed central basket baffle is designed, manufactured, operated, and developed for continuous catalytic DBT oxidation by the diesel desulfurization process. Also, process efficiency in a non-oscillatory baffled reactor is determined to show the important effect of oscillatory motion under the best conditions. The desulfurization process is examined using hydrogen peroxide (H_2O_2) as an oxidizing agent and a new synthesis of co-magnetic active oxides over activated carbon catalyst at mild process conditions. Also, the ODS kinetic model is used to estimate kinetic parameters for DBT oxidation reactions in diesel fuel.

2- Materials and experimental section

2.1. Materials

All used materials and their specifications are illustrated in Table 1. Feedstock is prepared by dissolving DBT in diesel fuel. The specified DBT concentration is 795 ppm. Diesel fuel properties are measured at the Kar Refinery in Erbil, Iraq.

2.2. Preparation of co-magnetic active oxides over activated carbon catalyst

Synthesis of co-magnetic active oxides over activated carbon catalyst (5% MnO_2–3% Fe_2O_3/AC) is satisfied by the incipient wetness impregnation (IWI) preparation method. 3.36 g of iron nitrate non-hydrate and 3.61 g of Manganese (II) nitrate tetra-hydrate are added and dissolved in 100 mL of pure deionized water (DW). Complete dissolution of salts is achieved by continuous mixing for 1 hr using an appropriate magnetic stirrer, resulting in a homogeneous solution. Then, 15 g of activated carbon is precisely weighed and added to the solution under ultrasonic homogenization for 2 hr. The formed solution is maintained in an oven for soft thermal drying (110 °C for 12 hr). A semi-solid mixture is produced after the drying step and then pushed into a tubular furnace for thermal calcination (N2 gas, 580 °C, 2 hr, heating rate of 5 °C/min). The thermal calcination process converts active metal salts into active oxides (MnO_2 and Fe_2O_3). Finally, a co-magnetic active oxide over activated carbon catalyst is formed and used in catalytic DBT oxidation experiments in an oscillatory and a non-oscillatory baffled reactor. Fig. 1 summarizes the preparation steps.

2.3. Characteristics of co-magnetic active oxide over activated carbon catalyst

The synthesis catalyst is examined by the following testing methods: Brunauer-Emmett-Teller (BET) to determine the textural properties (pore size, surface area, and pore volume), Scanning Electron Microscopy (SEM) to examine the surface structure and morphology, and X-ray Fluorescence (XRF) to observe the chemical composition of the prepared catalyst and metal oxide content.

2.4. Design, installation, and operation of the OBR unit

A new oscillatory baffled reactor is locally designed, installed, and operated for continuous catalytic Oxidation of DBT compounds in diesel fuel. A new central baffle has been developed by attaching central baskets rather than traditional central baffles to handle the solid catalyst. These central baskets not only provide efficient, uniform mixing conditions inside OBR but also ensure the necessary catalytic facilities, such as filling, emptying, and catalyst regeneration. The OBR setup is illustrated in Fig. 2 and is manufactured from stainless steel (316 grade). The geometrical dimensions of the new OBR design are as follows: the reactor height and inner diameter are 15.5 cm and 81 mm, respectively. New central baffles are geometrically designed as follows: 22 cubic baskets; a catalyst loading capacity of 4 g per basket; a basket diameter of 8 mm; a spacing of 2.33 cm between every two baskets; and a 0.3 cm-diameter central rod. A locally manufactured mechanical oscillatory pump generates oscillatory mixing. Oscillating parameters (frequency and amplitude) are regulated by changing the voltage and the plunger. Diesel oil and hydrogen peroxide are pumped co-currently at the bottom end of OBR via a dosing pump (MFG. NO. 5228, Taiwan) and a syringe pump (IML, Spain), respectively. An efficient heating jacket (0-600°C) is surrounded by an OBR tube to supply the desired reaction temperature. Glass wool is surrounded by an OBR column and a heating jacket to maintain the reactor temperature at the specified level (insulation). After completing the oxidation reaction, treated diesel is pumped from the top of OBR into the cooler, separator, and sulfur content analyzer.

Table 1. Materials and their specification

Material	Chemical structure	Specifications	Function	Provided by
Diesel fuel	Complex mixture	Specific gravity @15°C: 0.833, sulfur content: nil (9 ppm), Cetane Index: 53.9, Kinematic viscosity, mm^2/s: 3.15, and boiling range, °C: 165 - 357	Feedstock	Pendik Company, Turkey
Dibenzothiophene	$C_{12}H_8S$	Purity: 98%	Model sulfur compounds	Alfa Aesar Company, United Kingdom
Hydrogen peroxide	H_2O_2	Purity: 35%,	Oxidant	Merck Millipore Company, Germany
Activated carbon	Carbon materials	particle size range: 1 –3 mm		Applichem GmbH Company, Germany
Manganese (II) nitrate tetra-hydrate and ferric nitrate hydrate	$(MnN_2O_6.4H_2O)$ and $(Fe(NO_3)_3.9H_2O)$	Purity: 98%	Source for catalytic active metals oxides	Sigma-Aldrich Company, USA

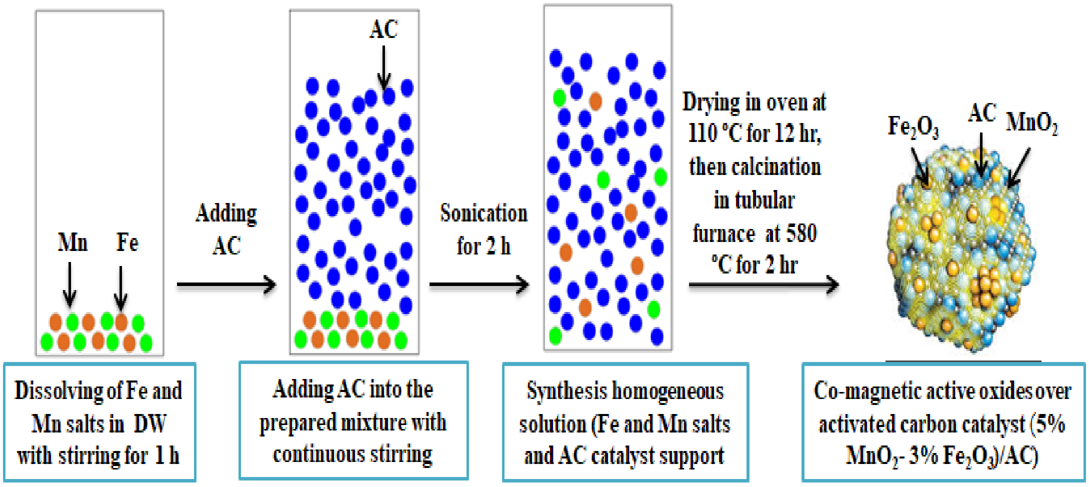

Fig. 1. The preparation steps of the composite catalyst

2.5. Desulfurization application in OBR

DBT (795 ppm) oxidation and removal from diesel fuel are evaluated using co-magnetic active oxides over an activated carbon catalyst (5% MnO_2–3% Fe_2O_3/AC) in a new design of an oscillatory baffled reactor. Hydrogen peroxide is employed as an oxidizing agent at an oxidant-to-DBT (O/DBT) molar ratio of 5. Oxidative desulfurization experiments of DBT are examined under the following mild conditions:

- Atmospheric pressure
- Oxidation times (3, 6, 9, 12) min.
- Oxidation temperatures of (30, 60, and 90) °C.
- Oscillation amplitude of (3, 6, 9, and 12) mm
- Oscillation frequency of (0.5, 1, 1.5, and 2) Hz

The new central baffles are filled with a co-magnetic active oxide synthesis over an activated carbon catalyst, and then the baffles are inserted and fixed inside the OBR column. Diesel fuel and Oxidant are fed co-currently from the storage tanks into the reactor bottom using a fuel dosing pump and an oxidant syringe pump, respectively, at the desired flow rates. Reactor temperature is maintained at the desired level by controlling the heater with the REX control system. Oscillatory mixing is created inside OBR by regulating the voltage and the plunger of the mechanical oscillatory pump. Thus, the DBT oxidation reaction is carried out until steady-state conditions are achieved. After completing the oxidation reaction (oxidation time is finished), treated diesel is fed into the cooler and then withdrawn from the top of the OBR column. After that, a diesel/aqueous mixture is produced and sent into the separation stage to separate the fuel phase from the aqueous phase. Pure diesel phase is sent into the X-ray sulfur analyzer, and the final DBT content is recorded. Each oxidation run is refined twice, and the average value is proven as the final DBT content.

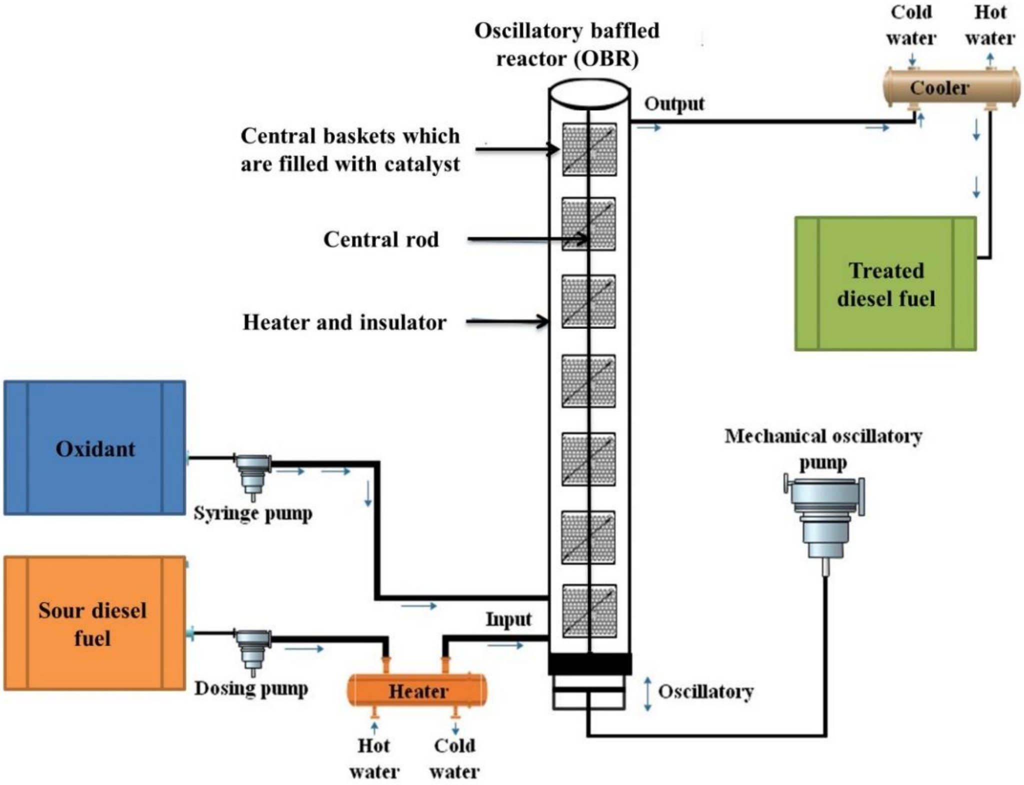

Fig. 2. Experimental setup for OBR

2.6. DBT content analysis

The DBT content of diesel as a feedstock or a clean product is examined by X-ray fluorescence (XRF) (Sindie-R2, Sindie Company, USA) according to ISO 20884 and ASTM D7039 test standards. DBT oxidation efficiency is evaluated based on Eq. 1.

$$\text{DBT oxidation efficiency (\%)} = \frac{C_{DBTin} - C_{DBTout}}{C_{DBTin}} * 100 \qquad (1)$$

Where, C_{DBTin}, C_{DBTout} are the initial and final DBT content in diesel fuel.

3- Results and discussions

3.1. Characterization of co-magnetic active oxides over activated carbon catalyst

N2 adsorption/desorption isotherm (BET test) is achieved to evaluate the texture characteristics (surface area, pore volume, and pore size) for activated carbon and the synthesis of co-magnetic active oxides over the activated carbon catalyst. BET results are illustrated in Table 2. Impregnation of AC via bi-active metal oxides (iron and manganese oxides) has significantly affected the textural properties of AC. The obtained data showed that the surface area decreased from 865 m^2/g for AC to 768 m^2/g for the new synthesis catalyst. A remarkable decrease in surface area can be attributed to the distribution of active oxides over activated carbon during the impregnation step. Also, pore volume is lowered from 0.524 cm^3/g (AC) to 0.487 cm^3/g (5% MnO_2–3% Fe_2O_3/AC) due to occupation of catalyst pores via the deposition of active oxides. On the other hand, the average pore diameter increases from 2.421 nm to 2.535 nm; this change can be attributed to the restructuring of smaller pores in the catalytic materials due to the effects of active oxide loading and calcination processes [40, 41].

Table 2. The texture properties for AC and co-magnetic active oxides over the activated carbon catalyst

Sample	**Surface areas m^2/g**	**Pore volumes cm^3/g**	**Pore diameters nm**
Activated carbon	865	0.524	2.421
Co-magnetic active oxides over activated carbon catalyst	768	0.487	2.535

N2 adsorption/desorption log isotherms for AC and co-magnetic active oxides over the activated carbon catalyst are shown in Fig. 3. The obtained data exhibit mixed isotherm behavior as follows [9, 42, 43].

- Strong adsorption/desorption pattern at low relative pressure (< 0.1), which proves a micro-porous structure for the used catalytic materials.
- Hysteresis loops at intermediate and high relative pressure, which can be assigned to the different rates of adsorption/desorption. This behavior is supported by micro- and medium-macro-pore structures in the catalytic materials.

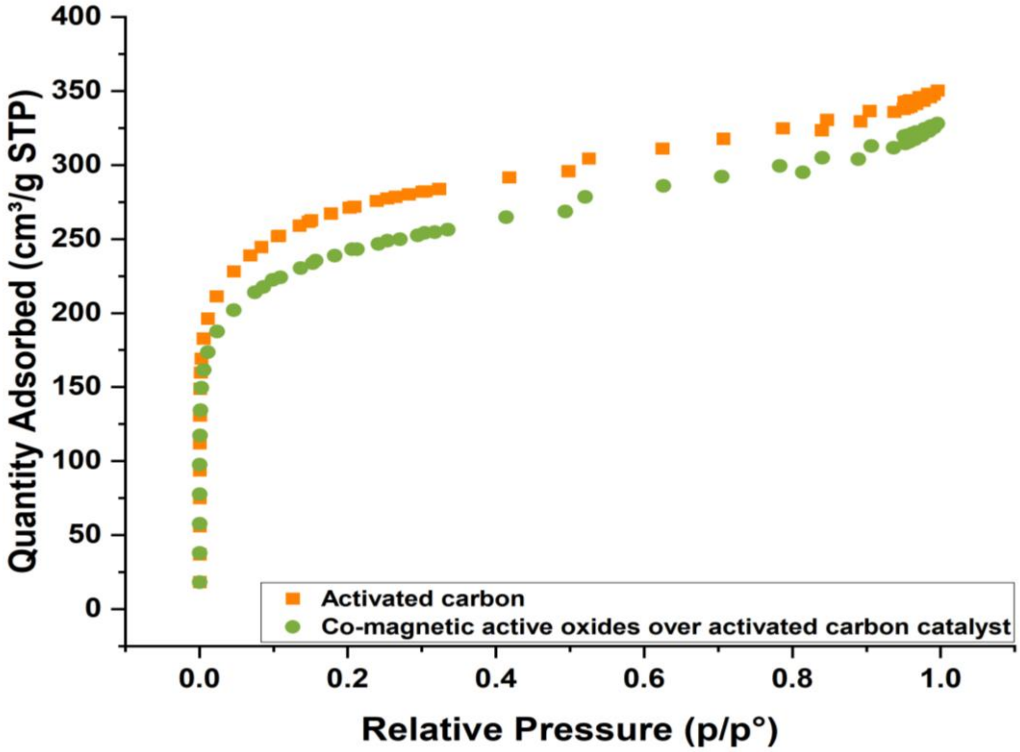

Fig. 3. N2 adsorption/desorption log isotherms for AC and co-magnetic active oxides over activated carbon catalyst

Surface structure and morphology for activated carbon and co-magnetic active oxides over the activated carbon catalyst are evaluated via SEM analysis. The obtained images are shown in Fig. 4. SEM images show a regular surface porosity of the used catalytic materials. The structure of the synthesis catalyst shows few cracks and cavities, which are formed during the thermal drying and calcination stages of catalyst preparation [44, 45]. Also, changes in the surface morphology of AC after loading active oxides indicate a uniform distribution of active metal oxides (iron and manganese oxides) over the activated carbon surface. Thus, the successful impregnation and loading of active metals onto AC are achieved, thereby yielding remarkable oxidation efficiency in the new oscillating reactor.

Fig. 5 shows the chemical composition, expressed as weight percent of the significant element oxides, as measured by XRF analysis of AC and synthesis catalysts. XRF data shows that AC is mainly composed of the following element oxides: 34.64 wt% of SiO_2, 12.25 wt% of Al_2O_3, 9.26 wt% of Fe_2O_3. Also, small amounts of other metal oxides, such as P2O5, MgO, TiO2, and K2O, are observed. These results agree with the main composition of AC and prove that it is catalytically active and thermally stable [9, 13, 46, 47]. XRF results for the synthesis of co-magnetic active oxides over an activated carbon catalyst show the presence of MnO2 at 5.3 wt% and increased the amount of Fe_2O_3 from 9.26 wt% to 12.57 wt%. These data demonstrate that the new catalyst is successfully prepared in the desired amounts of active metal oxides (5% MnO_2–3% Fe_2O_3/AC) via an efficient impregnation process. Also, the presence of other metal oxides in the synthesis catalyst composition, such as MgO, P2O5, and TiO2, enhances the catalyst's acidic and redox properties [48, 49].

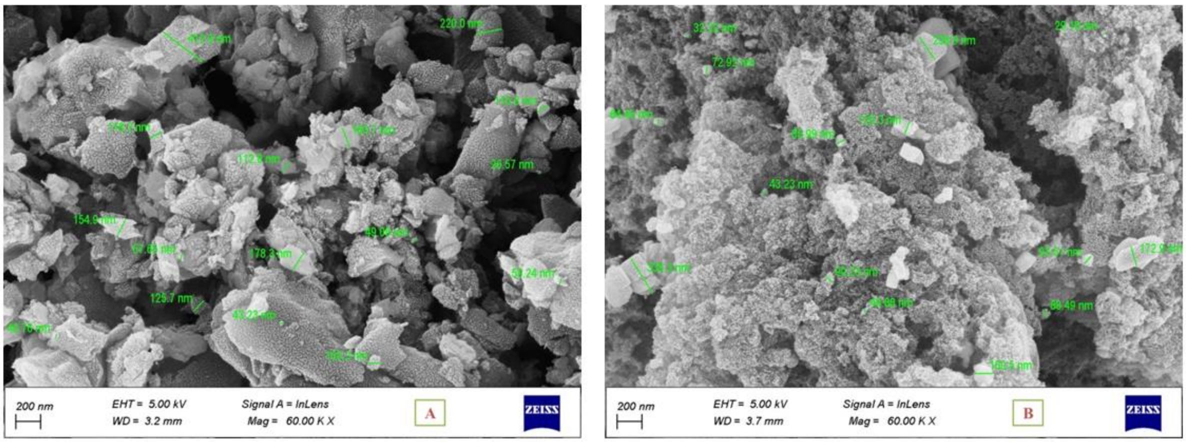

Fig. 4. SEM images for: (A) AC and (B) co-magnetic active oxides over activated carbon catalyst

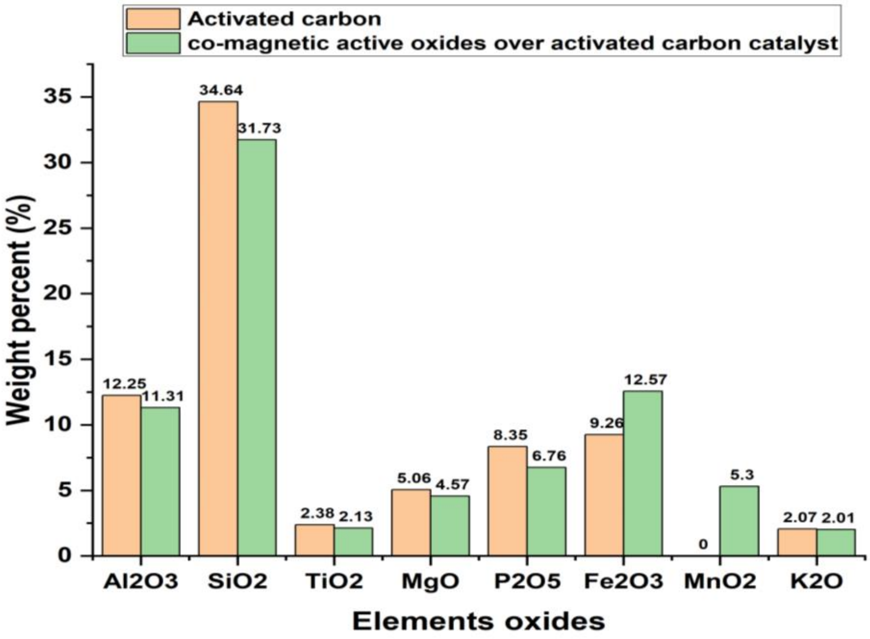

Fig. 5. XRF analysis for AC and co-magnetic active oxides over activated carbon catalyst

3.2. DBT oxidation performance

Fig. 6 (A and B) shows the effect of different oxidation times (3, 6, 9, and 12 min) and temperatures (30, 60, and 90 °C) on DBT oxidation efficiency using co-magnetic active oxides over activated carbon catalyst and hydrogen peroxide oxidant in the new oscillatory baffled reactor. The results show that increasing oxidation time and temperature significantly improve desulfurization efficiency. Increasing the oxidation time from 3 min to 12 min at f = 1 Hz, A = 6 mm, and T = 30 ◦C increases the desulfurization efficiency from 38.9 % to 75.2 %, as illustrated in Figure 6. A. Also, this figure shows that DBT removal efficiency increases from 58.7 % to 78.7 % as the temperature increases from 30 °C to 90 °C, at f = 1 Hz, A = 6 mm, and τ = 6 min. Figure 6B shows that DBT oxidation is improved from 82.4% to 98.1% with increasing oxidation time from 3 min to 12 min at T = 90 ◦C, f = 2 Hz, and A = 12 mm. Furthermore, enhance temperature from 30 °C to 90 °C is boosted DBT removal from 93.96 % to 98.1 % at τ = 12 min, f = 2 Hz and A = 12 mm.

Oxidation time has essential effect on DBT removal efficiency due to it is controlled the contact period between reactants, thereby more collision and interaction between reacting species is led to significant increase in oxidation performance. Also, increasing time has improved the reaction rate by altering the mass transfer rates of the reactants towards each other [33, 50-52]. As well as the combination of increasing oxidation time and the new design of baffles for the oscillating reactor forms an efficient hydrodynamic structure, lowered dead zones, improved regular flow distribution, produced uniform mixing, and upgraded mass and heat transfer rates, thus a dramatic enhancement in DBT oxidation efficiency is obtained as reaction time enhanced [33, 53].

Enhancing the oxidation temperature also significantly increases oxidation efficiency by improving oxidant decomposition to form active reaction species and enhancing mass transfer between H2O2 and DBT, thereby accelerating the oxidation reaction [22, 54-59].

Furthermore, an increase in temperature reduces the viscosity and density of diesel, leading to more vigorous mixing, collisions, and interactions between reactants, which significantly increases desulfurization efficiency [60]. The best DBT oxidation efficiency (98.1 %) is achieved at 90 ◦C for only 12 min in the new OBR.

The effect of oscillatory amplitude and frequency (oscillation conditions) on DBT oxidation efficiency is clearly shown in Fig. 7 (A and B). As shown in Figure 7A, DBT oxidation efficiency is boosted from 40% to 73.6% as the oscillatory frequency increases from 0.5 Hz to 2 Hz at τ = 3 min and T = 60 °C. Also, Figure 7B shows that increasing the oscillatory amplitude from 3 mm to 12 mm results in a significant increase in oxidation efficiency from 83.8% to 98.1% at τ = 12 min and T = 90 °C. Therefore, improving the oscillation mixing intensity has dramatically boosted the desulfurization efficiency based on the experimental data. This improvement can be attributed to the fact that enhancing the oscillatory mixing upgrades the oxidation kinetics, uniform mixing intensity, thermal distribution, mass and heat transfers, thereby enhancing desulfurization rates. Also, increasing frequency and amplitude are improved the number of oscillation cycles in unit time and their intensities, respectively, thereby vortices formation at OBR walls as well as cavities between each two central baskets baffles will be enhanced. Vortices formation is controlled the uniform mixing pattern inside OBR, thus enhancing it can be effectively improved DBT oxidation efficiency [33, 50]. As well as, increase the severity of oscillatory mixing is produced efficient interacting and reaction between DBT, H_2O_2, and synthesized catalyst, thereby remarkable desulfurization efficiency is satisfied [50]. Maximum desulfurization efficiency (98.1 %) is conducted at sever oscillatory conditions (f = 2 Hz and A = 2 mm).

A non-oscillatory baffled reactor (NOBR) is also operated by removing the effect of oscillatory flow (stopping the mechanical oscillatory pump) at the optimal operational parameters (90 ◦C and 12 min). This reactor is designed to assess the key impact of oscillatory mixing on desulfurization performance. Under the best conditions, experiments are achieved and compared at non-oscillatory conditions, soft oscillation (f = 0.5 and A = 3 mm), moderate oscillation 1 (f = 1 and A = 6 mm), moderate oscillation 2 (f = 1.5 and A = 9 mm), and severe oscillation (f = 2 and A = 12 mm), as illustrated in Fig. 8.

The results are clearly proved that the oscillating mixing is critical factor in boosting the efficiency of oxidation reactions, thus poor desulfurization rate (46.29 %) is achieved in absence the oscillatory flow under the effect of soft interaction between the laminar flow of fuel and reactor baffles in NOBR. Figure 8 shows that increasing the severity of oscillatory mixing dramatically enhances the oxidation efficiency, thereby increasing the desulfurization efficiency from 46.29 % under non-oscillatory conditions to 83.77 % (soft oscillation), 89.06 % (moderate oscillation 1), 94.59 % (moderate oscillation 2), and 98.11 % (severe oscillation).

These data demonstrate the remarkable influence of oscillatory flow on desulfurization efficiency, in contrast to the unobvious effect of net flow under laminar conditions. In NOBR, reactant mixing is produced only under laminar flow conditions (Ren < 35), resulting in soft mixing and inefficient contact between reacting molecules, leading to poor oxidation efficiency. Increasing the severity of oscillatory mixing in OBR significantly enhances the formation of adequate flow (vortices) and shear due to the interaction between the oscillatory flow of fuel and the central basket baffles, thereby boosting the coalescence and breakage of the reacting droplets and leading to fast oxidation reactions [39, 61].

Also, increasing the severity of oscillatory mixing increases vortex production, which is promising for radial mixing conditions [62]. Plug flow is achieved with efficient radial mixing and negligible axial mixing, thereby increasing oscillatory mixing and improving plug flow and desulfurization efficiency. In addition, increasing oscillatory flow enhances mass transfer, thermal distribution, and uniformity; as a result, rapid DBT oxidation is achieved.

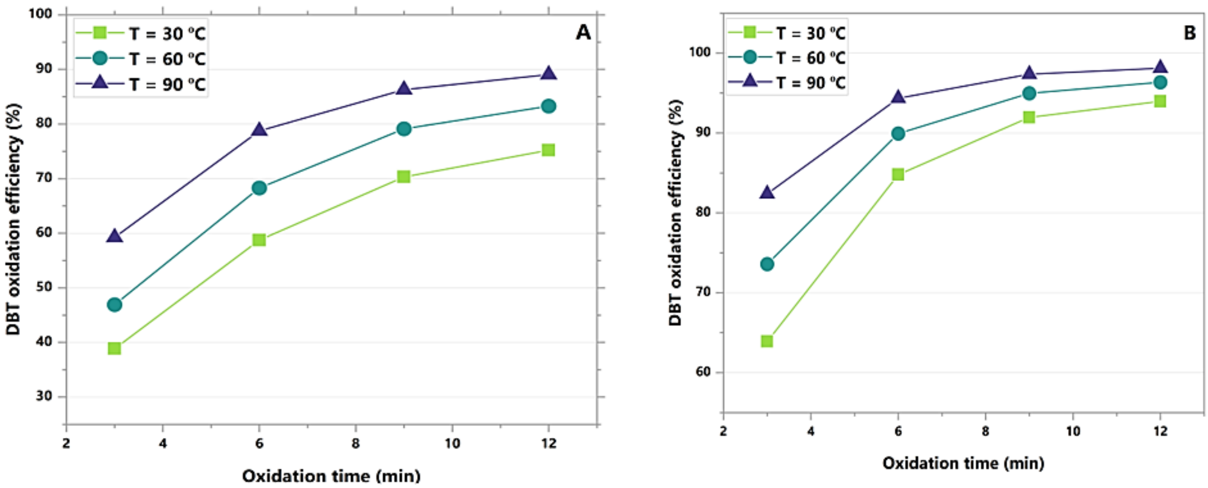

Fig. 6. Impact of oxidation time and temperature on DBT oxidation efficiency at (A) f = 1 Hz and A = 6 mm, and (B) f = 2 Hz and A = 12 mm

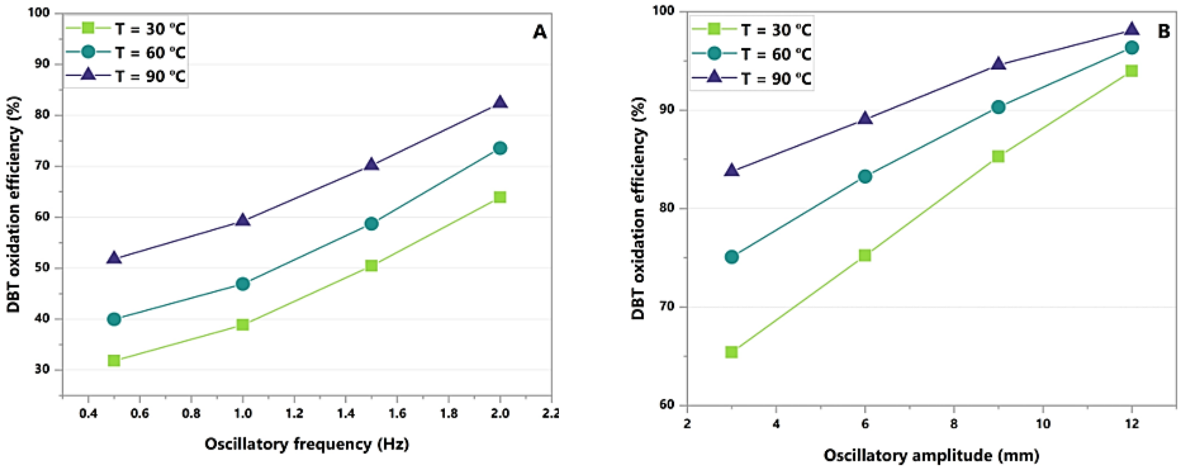

Fig. 7. Impact of oscillating parameters (A) Impact of frequency on DBT oxidation efficiency at τ = 3 min and (B) Impact of amplitude on DBT oxidation efficiency at τ = 12 min

The oxidation efficiency of DBT in diesel fuel using the new synthesized catalyst in the novel OBR design is compared with previous work, as summarized in Table 3. This comparison clearly demonstrates the novelty of the new design of the oscillatory baffled reactor, which packs solid catalyst particles in central baskets for continuous, deep desulfurization of dibenzothiophene in diesel fuel. Previous studies were conducted either in a batch OBR with a solid catalyst or in a continuous reactor with a liquid catalyst. Also, the synthesis of co-magnetic active oxides over activated carbon catalysts has been shown to have high activity for DBT removal, lowering sulfur content from 795 ppm to 15 ppm in only 12 min. This dramatic data can be returned to the efficient interaction between oscillatory flow or reactants and the new central baffles (baskets) in the presence of more catalytically active sites, thus uniform mixing and rapid improvement in the rates of mass transfer and desulfurization rate in a very short time are achieved, thereby remarkable DBT removal efficiency is satisfied compared to other desulfurization processes in OBRs.

4- The kinetic study of the ODS process in an OBR

Kinetic parameters for the oxidative desulfurization of DBT compounds in diesel fuel using co-magnetic active oxides over an activated carbon catalyst (5% MnO2-3 % Fe_2O_3/AC) in an oscillatory baffled reactor are experimentally investigated. The ODS kinetic model is determined under the best oscillating parameters (f = 2 Hz and A = 12 mm). The effect of oxidation time on DBT oxidation efficiency at different temperatures is summarized in Fig. 9. As shown, increasing oxidation time significantly enhances oxidation efficiency across all temperatures. This behavior can be assigned to enhance the interaction and collision time as oxidation time increases, leading to complete oxidation of DBT compounds in diesel fuel.

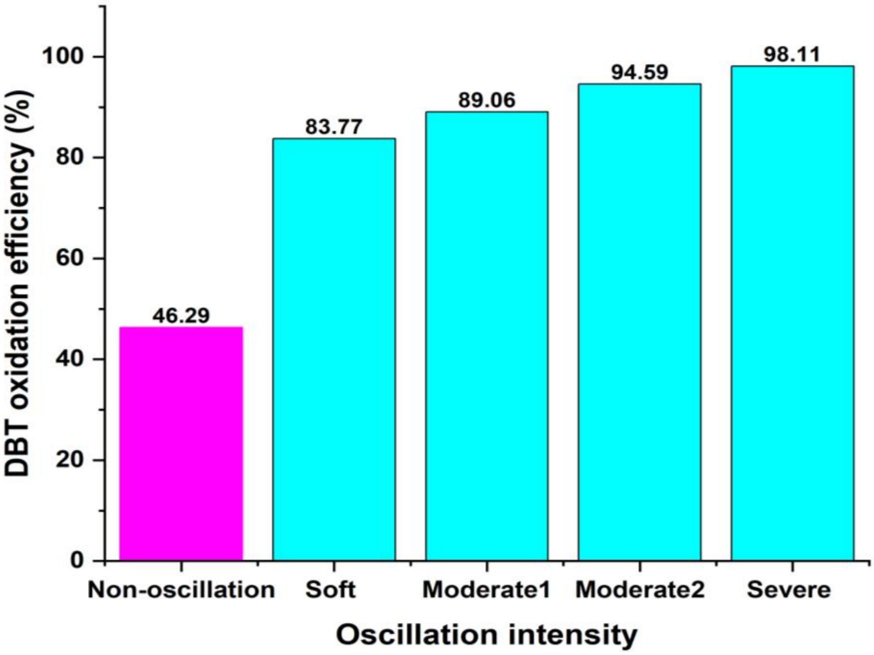

Fig. 8. Effect of oscillating mixing on DBT oxidation efficiency under the best conditions (90 ^{0}C and τ = 12 min)

Table 3. Oxidative desulfurization studies in OBR

Type of feedstock	**Sulfur content**	**Catalyst/ oxidant system**	**Type of reactor**	**Sulfur removal efficiency (%)**	**Reference**
Diesel fuel	569 ppm DBT	Acetic acid/ H_2O_2	Continuous oscillatory helical baffled reactor	94	[34]
Heavy naphtha	1091 ppm S	(Fe/ZSM-5)/O_2	Batch oscillatory helical baffled reactor	90	[37]
Diesel fuel	464 ppm DBT	(Fe_2O_3/γ-Al_2O_3–TiO_2)/ H_2O_2	Batch oscillatory helical baffled reactor	98.42	[63]
Diesel fuel	795 ppm DBT	(MnO_2- Fe_2O_3/AC)/ H_2O_2	Continuous oscillatory baskets central baffled reactor	98.11	Present work

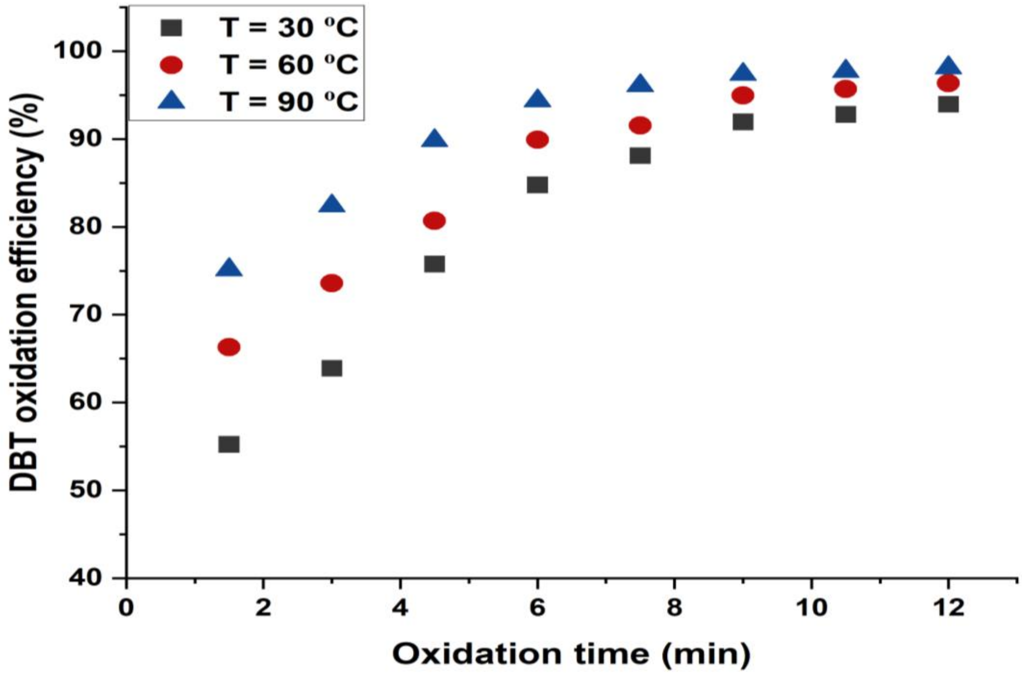

Fig. 9. The kinetics profiles of the DBT oxidation process in the oscillatory baffled reactor at f = 2 Hz and A = 12 mm

The integral method is applied to extract the kinetic parameters. The rate law for oxidative desulfurization reactions is:

$$-r_{DBT} = -\frac{dC_{DBT}}{dt} = k\,C_{DBT}^{n} \tag{2}$$

If the reaction rate follows first-order parameters (n = 1):

$$-r_{DBT} = -\frac{dC_{DBT}}{dt} = k\,C_{DBT} \tag{3}$$

Eq. 3 can be rearranged and integrated as follows:

$$-\int_{C_{DBTo}}^{C_{DBT}} \frac{dC_{DBT}}{C_{DBT}} = k\int_{0}^{t} dt \tag{4}$$

$$\ln\frac{C_{DBTo}}{C_{DBT}} = kt \tag{5}$$

Where r_{DBT} is the oxidation rate of dibenzothiophene (mol/l. min), *k* is the rate constant (min^{-1}), C_{DBTo} is the initial content of dibenzothiophene (mol/l) in feedstock, C_{DBT} is the final content of dibenzothiophene (mol/l) in treated oil, t is the desulfurization time (min), and *n* is the reaction order.

Based on Eq. 5, Fig. 10 shows the linear fitting analysis for DBT oxidation kinetics conducted with co-magnetic active oxides over an activated carbon catalyst (5% MnO_2- 3% Fe_2O_3/AC) in the new OBR. This figure proves that the DBT oxidation reaction follows a first-order kinetic model at different temperatures (30, 60, and 90 °C) °C with an R^2 of 0.977, 0.975, and 0.968, respectively. The desulfurization rate constants (k) are determined as follows: 0.20354 min^{-1}, 0.22981 min^{-1}, and 0.25923 min^{-1} at temperatures of 30°C, 60°C, and 90°C, respectively. The DBT oxidation reaction rate is well-followed first-order model through most previous desulfurization works, especially in the oscillatory baffled reactor [33, 50].

The apparent activation energy for the desulfurization reaction can be extracted based on the slope of the Arrhenius plot as follows:

$$k = k_0 e^{-\frac{E}{RT}} \tag{6}$$

$$-lnk = -lnk_0 + \frac{E}{RT} \tag{7}$$

Where T is oxidation temperature (K), R is the gas constant (kJ/mole. K), E is apparent activation energy (kJ/mol), and k_o is the Pre-exponential factor.

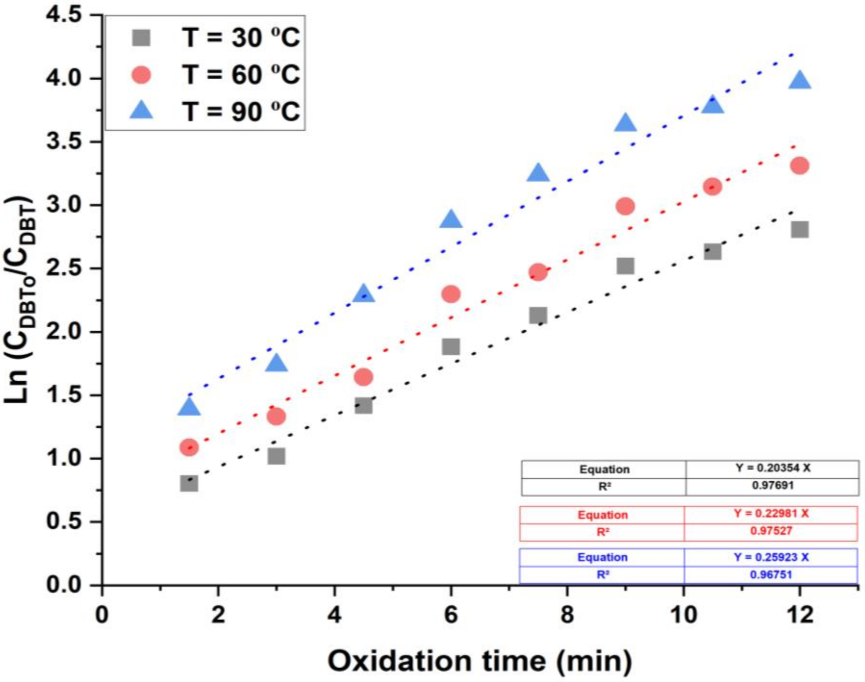

Fig. 10. First-order kinetic data at various temperatures (30, 60, and 90) ºC

Fig. 11 clearly shows the plot of (-ln k) vs. (1/T) and the linear fit of these data. The obtained data show that the activation energy (E) and the pre-exponential factor (ko) of the desulfurization reaction in OBR are 3.68 kJ/mol and 0.369 min^{-1}, respectively. The low activation energy indicates that the DBT oxidation technology proceeds rapidly with a lower required energy. These findings agree with the experimental short oxidation time (12 min) required to achieve maximum removal efficiency (98.1%). Also, this behavior can be assigned to increase the electron density of DBT, thereby resulting in a dramatic reduction in the activation energy [64, 65]. Thus, low activation energy is attributed to oxygen electrophilic addition or to high electron density on dibenzothiophene compounds [66]. A low value of the pre-exponential factor indicates that DBT oxidation reactions are non-spontaneous in OBR[67].

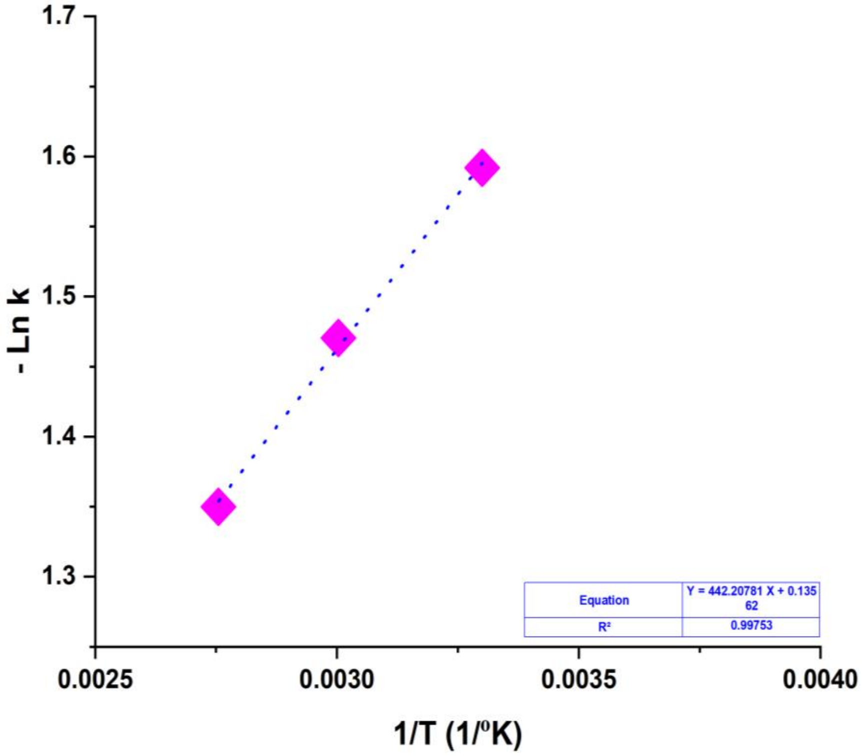

Fig. 11. Estimation of activation energy and pre-exponential factor based on Arrhenius plot

5- Suggested mechanism for oxidative desulfurization reaction of DBT in OBR

The essential impact of catalyst or oxidant availability during the DBT oxidation reaction is examined under optimal operational parameters (T = 90 °C, τ = 12 min, frequency = 2 Hz, and amplitude = 12 mm). As shown in Fig. 12, the results demonstrate that DBT removal efficiencies are very low in the absence of a catalyst or an oxidant; thus, both are indispensable. The catalytic role of manganese and iron oxides, their incorporation with high-surface-activated carbon, in boosting the rate of desulfurization reactions is attributed to their ability to provide more catalytically active sites and enhance sulfur adsorption capacity [68]. Also, the combination of MnO_2 and Fe_2O_3 as co-active components modifies the structure of catalytic pores and affects the surface chemistry of the support (AC), thereby forming new functional groups and enhancing adsorption and catalytic behavior [69].

Fig. 13 summarizes the suggested mechanism for oxidative desulfurization reaction of DBT compounds using co-magnetic active oxides over activated carbon catalyst (5% MnO_2- 3% Fe_2O_3/AC) in OBR. The desulfurization mechanism can be summarized as follows: first, DBT compounds are transferred by diffusion from the bulk fluid (diesel) to the catalyst surface, and then they diffuse into the interior catalytic pores. After that, it is contacted and attached to the active oxides (Fe_2O_3 and MnO_2). Hydrogen peroxide molecules are also diffused into the interior pores, where they interact with DBT compounds at catalytically active sites. The combined impact of atomic electron density for active oxides and oxygen vacancies causes fast adsorption of oxidant species by coordinating the peroxy O-O bonds, enhancing O-O bond breakage, and boosting the formation of active electrophilic OH routes [70-72].

Hydrogen peroxide can be decomposed into $O^{\cdot}$ (mainly via ODS reactions) or ·OH, with water molecules rejected as a green byproduct. At the oxidation stage, DBT is partially oxidized to form sulfoxide (DBTO), which is then completely oxidized to generate sulfones (DBTO2) [26, 58, 73]. After the oxidation step, the water produced by hydrogen peroxide decomposition serves as the aqueous phase for the extraction stage. Then, DBTO/DBTO2 are migrated from the diesel phase into the aqueous phase [33, 34]. Finally, friendly, environmentally friendly diesel fuel is formed as the final clean oil.

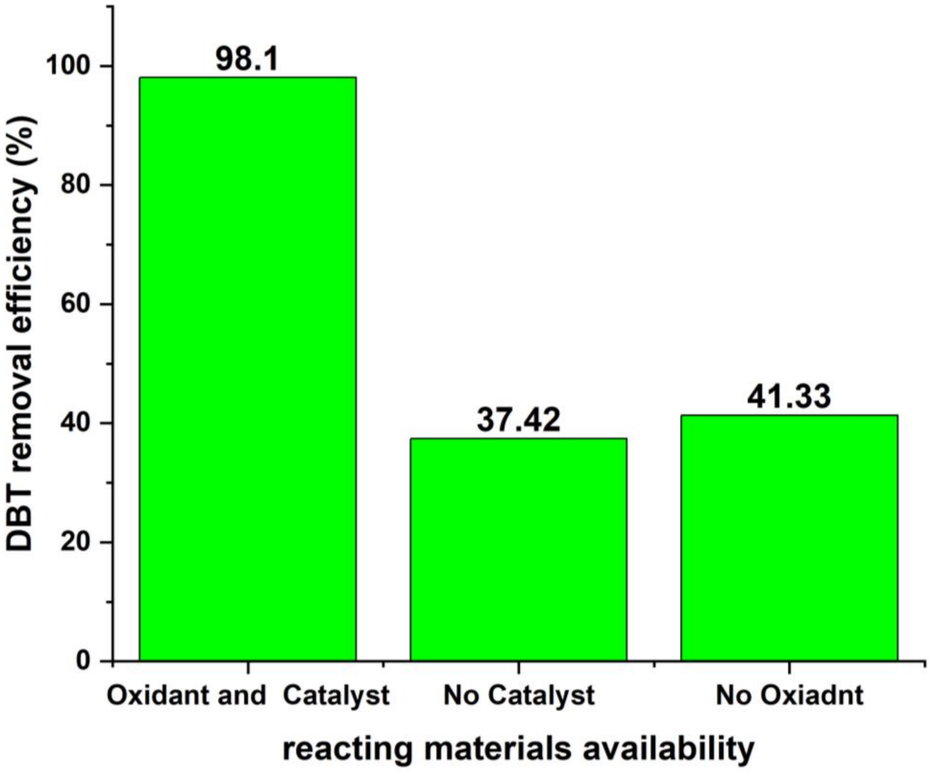

Fig. 12. DBT oxidation reactions without oxidant or without catalyst

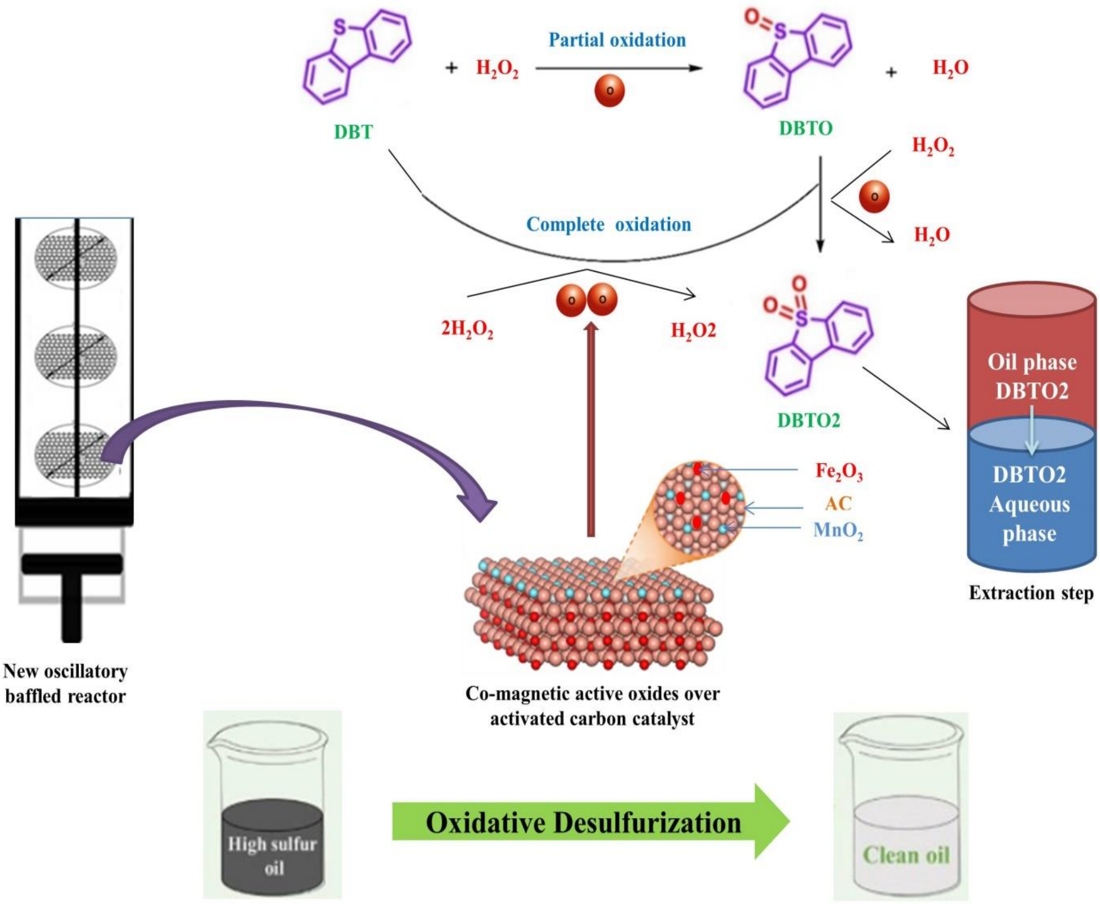

Fig. 13. Suggested mechanism for DBT oxidation reactions using co-magnetic active oxides over activated carbon catalyst (5% MnO_2- 3% Fe_2O_3/AC) in OBR

6- Conclusion

In this study, oxidative desulfurization reactions for removing DBT compounds from diesel fuel are examined using newly synthesized co-magnetic active oxides over an activated carbon catalyst (5% MnO2-3 % Fe2O3/AC) in a novel oscillatory baffled reactor design. OBR is developed by replacing the traditional central baffle with a central basket baffle to pack catalyst particles in a fixed bed for continuous, deep desulfurization. Also, the combination of manganese and iron oxides as co-active components over high-surface-activated carbon has modified the structure of catalytic pores and the surface chemistry of the catalyst, thus forming new functional groups that enhance the catalyst's reactivity towards the fast removal of DBT compounds.

Desulfurization reactions are conducted using hydrogen peroxide as oxidant under different conditions: temperature (30 - 90) °C, oxidation time (3–12 min), oscillatory frequency (0.5 - 2) Hz, and oscillatory amplitude (3 -12 mm). DBT removal efficiency is enhanced by increasing all operational parameters. Maximum DBT oxidation efficiency (98.1 %) is satisfied under the best experimental parameters (90 °C, 12 min, 2 Hz, and 12 mm). The kinetic model is determined under the best parameters in the oscillatory baffled reactor. Oxidative desulfurization reactions are described by a first-order model with a low activation energy (3.68 kJ/mol). These findings demonstrate that DBT oxidation in the new OBR is a cost-effective, eco-friendly process, producing high-value, clean diesel fuel oil with a short reaction time and minimal energy requirements.

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دراسات حركية و توصيف لإزالة الكبريت بالأكسدة من وقود الديزل النموذجي في مفاعل متذبذب ذو حاجز باستخدام أكاسيد نشطة مغناطيسية مشتركة فوق محفز الكربون المنشط

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الخلاصة

تحظى عملية إزالة الكبريت بالأكسدة (ODS) باهتمام كبير في المجالين الأكاديمي والصناعي، وذلك لتلبية التشريعات البيئية الصارمة الجديدة وإنتاج وقود صديق للبيئة. يتناول هذا البحث إزالة الكبريت بالأكسدة التحفيزية لمركبات ثنائي بنزوثيوفين (DBT) من وقود الديزل باستخدام أكاسيد نشطة مغناطيسية مشتركة فوق محفز الكربون المنشط (Fe_2O_3 + MnO_2/AC). تُجرى تفاعلات أكسدة DBT في مفاعل جديد ذي حاجز تذبذبي وغير تذبذبي (OBR وNOBR). طُوّرت حواجز سلال مركزية جديدة للتعامل مع جزيئات المحفز كحشوة ثابتة في OBR لأول مرة. تُفحص عملية ODS باستخدام بيروكسيد الهيدروجين كمؤكسد في ظل معايير تشغيل مختلفة: درجات الحرارة: ٣٠–٩٠ درجة مئوية، أوقات الأكسدة: ٣–١٢ دقيقة، التردد: ٠,٥–٢ هرتز، والسعة: ٣–١٢ ملم. أظهرت النتائج تحقيق أعلى كفاءة لإزالة الكبريت (٩٨,١%) في أفضل الظروف (٩٠ درجة مئوية، ١٢ دقيقة، ٢ هرتز، و١٢ ملم) في OBR. ويعود السبب الرئيسي لأكسدة DBT الشديدة في زمن إزالة الكبريت القصير إلى التأثير المشترك الجذاب للتدفق التذبذبي والنشاط العالي للمحفز المُصنّع. وقد فُحص نموذج حركية إزالة الكبريت في أفضل الظروف. وأظهرت النتائج الحركية أن تفاعلات ODS تتبع نموذج الدرجة الأولى. كما حُددت طاقة تنشيط منخفضة (٣,٦٨ كيلوجول/مول)، مما يُثبت سرعة أكسدة DBT عند طاقة مطلوبة أقل.

الكلمات الدالة: أكسدة DBT، محفز مشترك، كربون نشط، مفاعل حاجز تذبذبي، معلمات حركية.