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Investigation Desulfurization Method Using Air and Zinc Oxide/Activated Carbon Composite

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Abstract

In present work examined the oxidation desulfurization in batch system for model fuels with 2250 ppm sulfur content using air as the oxidant and ZnO/AC composite prepared by thermal co-precipitation method. Different factors were studied such as composite loading 1, 1.5 and 2.5 g, temperature 25 °C, 30 °C and 40 °C and reaction time 30, 45 and 60 minutes. The optimum condition is obtained by using Tauguchi experiential design for oxidation desulfurization of model fuel. The highest percent sulfur removal is about 33 at optimum conditions. The kinetic and effect of internal mass transfer were studied for oxidation desulfurization of model fuel, also an empirical kinetic model was calculated for model fuels at optimum condition, the apparent activation energy was found to be 16.724 kJ/mol.

Key words: Oxidation desulfurization; Model Fuel; Kerosene; Taguchi method; ZnO/AC composite; Air Oxidation.

Introduction

Petroleum refining industry has problems in production of low sulfur fuel as the new specification in the world [1]. The present records of the sulfur containing compounds in the fuel products available for use are as high as 3000 ppm while the past universal regulation is about 500 ppm [2] and current regulation is about 50 ppm [3] and for future new limit is less than 15 ppm [4]. The oxidation desulfurization is expected to solve great environmental problems occurring wherever different petroleum fractions are used. Odor and toxic emissions due to the combustion of these fuels producing gases are expected to be reduced to low levels.

Hydrodesulfurization (HDS) processes are used for removing aliphatic sulfur (RSR) and acyclic sulfur compounds such as dimethylsulfide, diethylsulfide, dibutylsulfide, diphenyl sulfide, thianisole, dibenzyl sulfide…etc. and less effective for the removal of cyclic sulfide such as thiophene, benzothiophene, dibenzothiophene, and 4, 6-methyl diabenzothiophene. In addition to HDS process cannot exceed the 100 ppm of sulfur content although with severe conditions [5].

Technologies that do not used hydrogen for catalytic decomposition of organosulfur compounds are discussed as a non-HDS based desulfurization technologies, also these processes may be adopted as ultra-fine deep desulfurization for many petroleum fractions. Direct selective oxidation of organosulfur compounds to sulfone, using oxygen or air rather than hydrogen to remove sulfur from refinery streams is attractive due to the availability of the reacting gas and its low price[5].

Mild conditions of ODS process, the temperature is ranged 40-100 ^oC and pressure is ranged is 1- 2 bar [1] and also sometimes using room temperature and atmospheric pressure, made this process economic and novel, since the refractory sulfur compounds which are not removed in HDS process can be oxidized to sulfones that removed by adsorption and extraction [6].

The main objective of the oxidant is to oxidize sulfur compounds from a fuel sample to corresponding sulfides or sulfones by adding electrophilic oxygen atom that converts sulfur compounds to polar form[7].

Murata, S. et al., (2004) examined ODS model diesel (DBT and benzene) fuel with sulfur content 3300 ppm and commercial diesel fuel with sulfur content 193 ppm by using aldehydes (n-octanol, n-hexanol, n-decanol and benzaldehyde) with molecular oxygen was examined in the presence of transition metal salts (cobalt, manganese, and nickel salts), the aldehydes oxidize by metal oxide to produce peracids and then DBT oxidize to sulfones by using peracids generated as a catalyst, sulfones can removed by extraction with polar solvents (acetonitrile), adsorption (silica or alumina) or/and extraction, with extraction by acetonitrile reduce sulfur content is 36 ppm ,Adsorption over 20 g silica the sulfur reduction is 19 ppm and adsorption over 60 g alumina the sulfur reduction content to <5 ppm [8].

Ma et al., (2007) studied ODS of a model jet fuel (BT, 2-MBT, 5-MBT and DBT dissolved in n-Decane) with sulfur content 412 ppm reduce to 2 ppm and a real jet fuel (JP-8) with sulfur content 717 ppm reduce to 126 ppm with molecular oxygen at ambient condition and an adsorption using Fe (III) nitrate and Fe (III) bromide with and without carbon support and also over an activated carbon [5].

Sundaraman, et al., (2010) studied the of ODS of commercial jet fuel (JP-8-520) with 520 ppm and commercial diesel fuel (LSD-41) with 41 ppm by using air as an oxidant for generating hydroperoxides with CuO as catalyst, and it was used to oxidize the sulfur compounds to sulfones around 99% and 80% of sulfur compound is oxidize in jet and diesel fuel respectively with MoO_3/SiO_2, then the sulfone formed is adsorbed by Beta zeolite to ultra-low sulfur jet and diesel fuel [4].

Imtiaz, et al., (2013) studied ODS of model oil (thiophene, DBT, and 4-MDBT dissolved in n-heptane) with sulfur content 1275 ppm reduced to 57 ppm, and commercial oil (untreated naphtha, light gas oil, heavy gas oil and Athabasca) using an air-assisted performic acid oxidation with phase transfer catalyst (emulsion catalyst). Sulfur removal rate for commercial oil including untreated naphtha was 83%, light gas oil 85%, heavy gas oil 68% and Athabasca 64% [9].

Nawaf, et al., (2015) studied ODS of DBT in light gas oil (LGO) initial sulfur content 1000 ppm, in trickle bed reactor with homemade manganese oxide ($MnO_2/\gamma\text{-}Al_2O_3$), the highest removal was 81.2% (188 ppm) at 200°C [10].

This study can be applied as complementary process to hydrodesulfurization which can have an important role in producing fine or ultrafine fuel like gasoline or kerosene. In a cost point of view, this study is focusing on the use of local available materials or the conversion of these materials into new ones which are more effective.

In present work zinc oxide loaded on activated carbon was studied with oxidation desulfurization of model fuel in presence of air as an oxidant in batch system. The design of experiments by the Taguchi method was considered to find the optimum conditions, these optimum conditions examined with the Iraqi kerosene in the same systems.

Experimental

1. Materials

Kerosene with sulfur content 2850 ppm was supplied by the Midland Refineries Company/Al-Dura Refinery, and the model fuels dibenzothiophene $C_{12}H_8S$ with purity 99% was supplied by Himedia, India, dissolved in n-nonane with purity 99% was supplied by BDH Chemicals, England. Activated carbon was supplied by Thomas Baker/India, zinc nitrate hexahydrated $Zn(NO_3)_2.6H_20$ with purity 98% was supplied by Thomas Baker, India and sodium hydroxide with purity 99% pellets was supplied by Hopkin and Williams, England.

2. ZnO/AC Composite Preparation

Zinc oxide loaded on activated carbon composite is prepared in thermal co-precipitation method. Activated carbon is dried in oven for 1 h at 200 °C; to remove moisture. Weighted 5 g of activated carbon powder and dispersed in 125 ml deionized water. This solution consisting of AC with deionized water was mixed by magnetic stirrer plate for one day for best dispersion. 0.9325 g of zinc nitrate hexahydrate was dissolved in 13 ml deionized water to obtain approximately 10 wt. % loading of ZnO. Then Add Zinc nitrate solution slowly with mixing. The pH adjustment of the mixture was done by adding 1M of NaOH solution until the pH reaches 8-9. The mixture was heated for 6 h at 90°C by reflux with stirring. The product was cooled then filtrated by vacuum pump, washed, dried at 110 °C overnight and calcined the product for 3h at 250 °C.

3. Experimental Procedure

The model fuel in present work is n-nonane with sulfur content of 2250 ppm made by dissolving appropriate amount of DBT. The ODS experiments were carried out in 250 ml flask; air was bubbled at constant flow rate. UV-spectrophotometer instrument (Genesys 10 UV) was used to calculate the concentration of DBT in n-nonane at 325 nm wave length. Figure 1 shows the UV- calibration curve for concentration of DBT. The sulfur content of kerosene filtered was determined according to ASTM D-7039 in the Petroleum Research and Development Center / Ministry of oil by using the testing device (Sulfur analyzer, Sindie OTG, USA).

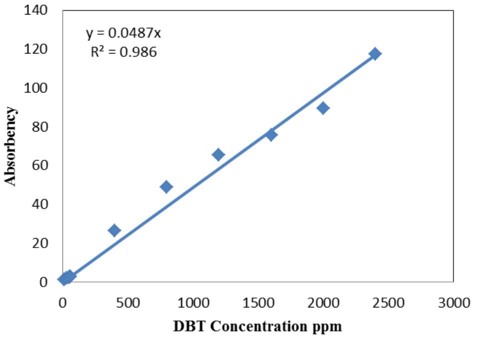


Fig. 1: UV-calibration curve

4. Characterization

The crystalline phase of zinc oxide on the surface of activated carbon were examined by X-ray using CuKα radiation (λ=1.54056A). Data were collected within the 2θ range of 20^o and 80^o. The phase identification was achieved by comparing with reference data from the International Center for Diffraction Data (ICDD). XRD analysis was performed on Bruker, D2 phaser (German 2010) and achieved in Iraqi-German Lab.

The amount in weight percent of zinc oxide in prepared composite was determined by X- ray Florescence using Spectro XEPOS (German 2010). XRF analysis was achieved in Iraqi-German Lab.

Determination of prepared composite surface area and pore volume was achieved at Petroleum Research and Development Center / Ministry of Oil using BET method by Thermo Finnegan type, apparatus. BET surface area measurements were made by measuring N_2 adsorption, the degasing temperature 200 ^oC for 1 h.

Atomic Force Microscopy gives the topography with high resolution by determining the interaction forces between the surface and a sharp tip mounted on a cantilever Atomic force microscopy was achieved in Chemistry Science Department / Collage of Science / University of Baghdad. (SPM-AT 3000 / Atomic force microscopy / Angstrom-Advance Inc., USA 2008 / contact model).

Results and Discussion

1. Characterization of ZnO/AC Composite

The XRD patterns of the raw activated carbon, showed the peaks of 2θ between 20-30 and 40-50, which is noisy disorderly indicates to amorphous carbon as shown in Figure 2. Also, found in literature [11].

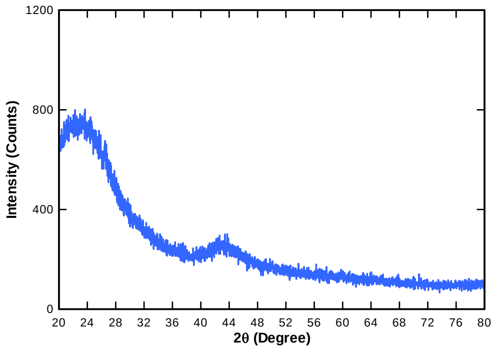


Fig. 2: XRD Pattern of activated carbon

For AC/ZnO, the clear peaks at 2θ of 34.438, 36.249 and 47.539 shown in Figure 3 indicates a crystalline ZnO, and noisy background patterns refer to amorphous carbon.

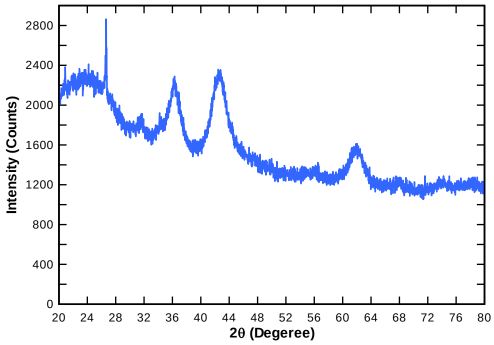


Fig. 3: XRD Pattern of AC/ZnO

The XRF analysis shows the metal oxide composition for zinc oxide loading on the surface of the activated carbon. A measured zinc oxide was approximately 10 wt. %. The loading ratio was chosen 10 wt.% because the increasing in loading ratio causes the block of pore, and leads to decrease of surface area [12].

The surface area of prepared ZnO/AC composite was measured by BET method; the resulted values of surfaces area and pore volume are listed in Table 1.

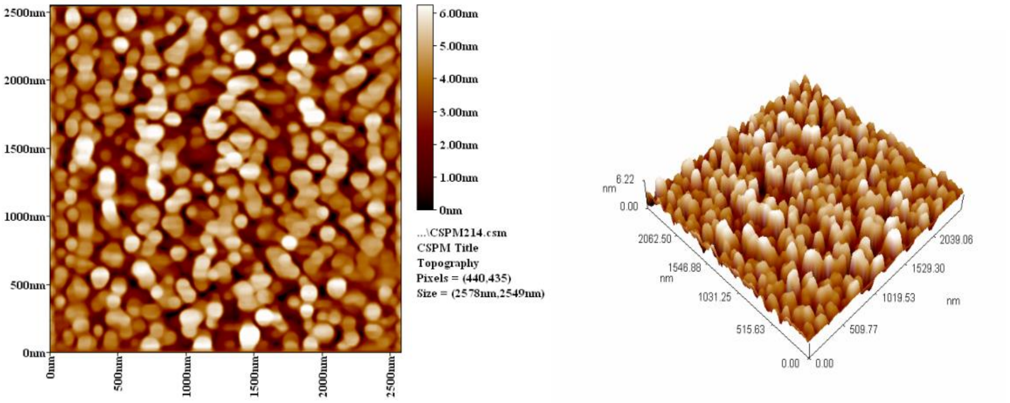
Table 1: Surface Area and Pore Volume

Property	AC	ZnO/AC
Surface Area, m^2/g	1005.5045	972.72
Pore Volume, cm^3/g	0.6203	0.6114

A slight decrease in surface area of activated carbon was observed after loading of approximately 10 wt. % zinc oxide as listed in Table 1. Since the surface area is still high and near to the values of the original source, and sometimes the surface area and pore volume increase or be the same or near from original source in case of loading ratio less or equal 10 wt % , this is due to good dispersion of the metals oxides[13]. The average particle size was determined by AFM. Table 2 list the particles size distribution of activated carbon and ZnO/AC composite. Figure 4 shows topographical surface images of activated carbon and ZnO/AC in two dimensional (2D) and three dimensional (3D) were obtained from AFM analysis.

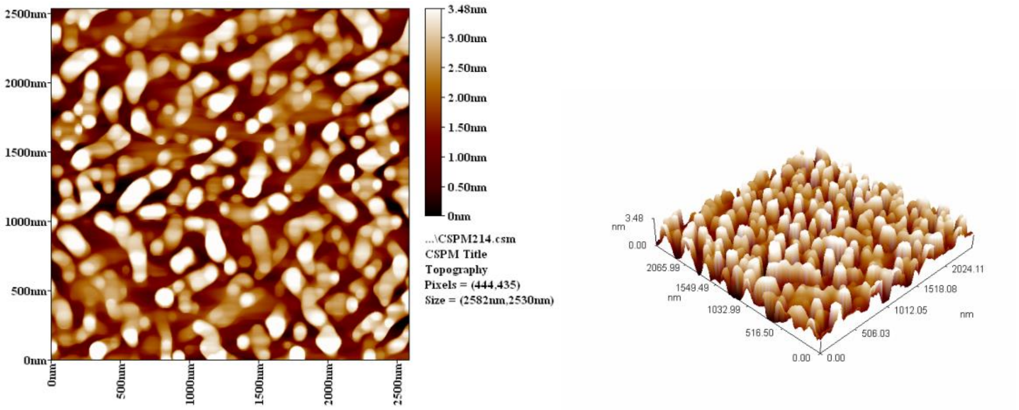
Table 2: Particle Size Distribution

Composite	Avg. Diameter (nm)	≤ 10vol % (nm)	≤ 50vol % (nm)	≤ 90vol % (nm)
AC	93.84	50	90	140
AC/ZnO	104.72	60	90	150



a) 2D AC surface

b) 3D AC surface



c) 2D ZnO/AC surface

d) 3D ZnO/AC surface

Fig. 4: AFM Test

2. Analysis by Taguchi Method

The Taguchi method used to analysis the result by using Mintab 17, the results are statistically using signal to noise ratio (S/N). Different factors such as composite amount, temperature and time have been studied in order to find the optimum conditions for ODS by air using ZnO/AC. Table 3 lists the nine runs experiments with its results. S/N Ratio is calculated using Minitab 17. In the present work, S/N ratio the larger is better is considered. A larger S/N ratio corresponds to the best level condition. Figure 5 shows effects of S/N ratio for all levels.

Table 3: Results of Taguchi experiment design for removal of sulfur compounds

Composite Amount, g In 100 ml n-nonane	**Temperature, ^{o}C**	**Time, min**	**Concentration, ppm**	**% Removal**	**S/N Ratio**
1	25	30	1834.692366	18.45811707	25.3237
1	30	45	1660.432628	26.20299429	28.3670
1	40	60	1774.630416	21.12753707	26.4970
1.5	25	45	1702.956489	24.31304493	27.7168
1.5	30	60	1648.340156	26.74043752	28.5434
1.5	40	30	1797.85437	20.09536133	26.0619
2.5	25	60	1527.976008	32.0899552	30.1274
2.5	30	30	1621.592567	27.92921923	28.9212
2.5	40	45	1613.263977	28.29993788	29.0355

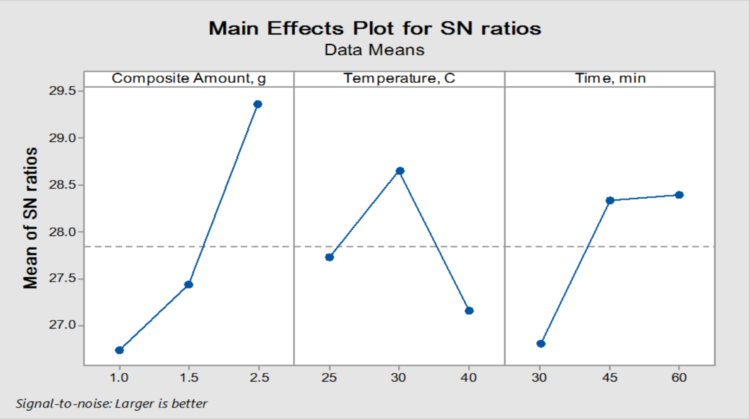


Fig. 5: Main effect Plot of S/N ratios

According to Figure 5, the best levels can be determined depending on the lager value of S/N ratio, so that, the optimum conditions are composite loading 2.5g, 30 ^{o}C and 60 min. The order of effect of the factors is composite amount>Time (min) Temperature (^{o}C). Figure 6 illustrates the percentage contribution of individual variables on variation in % sulfur removal.

The amount of zinc oxide/ activated carbon have the highest effect compare to other, this because of increase of active surface area that adsorption the sulfur compounds as shown in Figure 7.

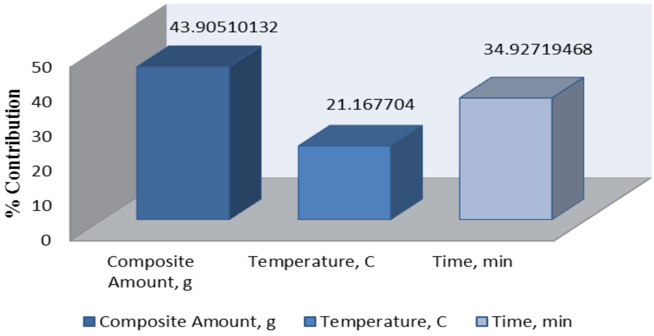


Fig. 6: Percentage Contributions of Individual Variables

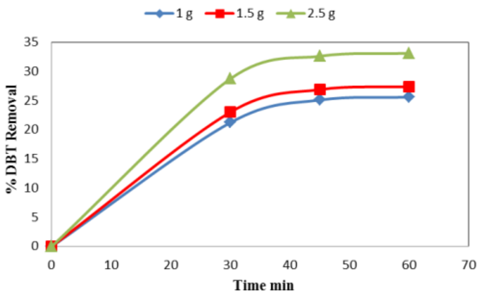


Fig. 7: Effect of Composite Amount on DBT Removal

The temperature has the lowest effect compare to the effects of other factors, since the increasing temperature in present systems leads to loss of solvent as shown in Figure 8.

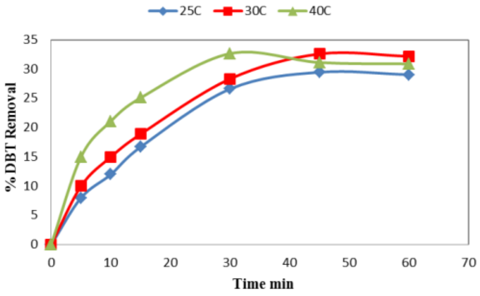


Fig. 8: Effect of Temperature on DBT removal

As the time increase the DBT removal increase due to increase amount of sulfur compounds remove, above 45 min, the sulfur removal slow decreases, which can be explained by reaching the maximum capacity as shown in Figure 8. The sulfur compounds converts to corresponding sulfones that is more adsorbed than sulfides. The hydroperoxides that convert sulfide to sulfone increases as the time of process increase.

The regression Equation 1 that describes the general linear model for the present system obtained from analysis results by Mintab 17 is:

$$\%DBT\ Removal= 25.028 +X_{i1}+ X_{i2}+ X_{i3} \qquad \ldots(1)$$

The values of X_{i1}, X_{i2} and X_{i3} for each factor and level are listed in Table 4. X_{i1} represent the amount of composite for level i, X_{i2} represent the temperature for level i and X_{i3} represent time for level i. The R^2 value for L9 run is 0.9648 which confirms a high quality agreement between the experimental and predicted values. The confirmation of model by comparison between DBT removal at best conditions of experiment and model equation, the experimental sulfur removal is 33% and the predicted is 33.115% gives the percent error is 0.3473%.

Figure 9 shows the relationship between experimental responses versus predicted.

Table 4: Coefficient values of Regression Equation

Factors	Levels		
	1	2	3
X_{i1}	-3.099	-1.312	4.411
X_{i2}	-0.075	2.052	-1.98
X_{i3}	-2.744	1.120	1.624

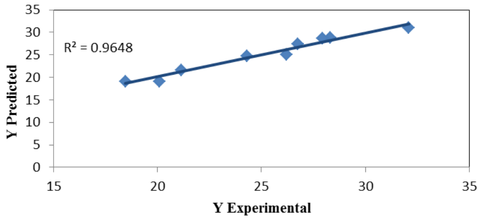


Fig. 9: Experimental versus Predicted Response

3. ODS of Kerosene Fuel

The kerosene fuel in present work with sulfur content 2850 ppm conducted ODS experiments in same batch system at optimum conditions from Tauguchi method analysis of model fuels (2.5g ZnO/AC, 30 ^{o}C and 60 min, the samples was test after filtered from composite. the total sulfur content determined is 2200 ppm, the sulfur removal percent 21% is less than model fuels at the same conditions because of the kerosene fuel contains in addition to sulfur compounds other aromatic compounds that have the same skeleton of sulfur compounds, this leads to decreased the selectivity to sulfur compounds [5].

4. Kinetic Model for Model Fuel

In present work, the kinetic model of ODS by using air and zinc oxide/activated carbon was examined by pseudo-first order and pseudo second order kinetic rate equation to find the best kinetic model by comparison between correlation coefficient R^2. Equations) represent the pseudo first order kinetic and Equation 3 represents pseudo second order kinetic.

$$\ln \frac{C0}{Ct} = kt \qquad \dots (2)$$

$$\frac{1}{Ct} = \frac{1}{Co} + kt \qquad \dots (3)$$

Figure 8 shows the effect of time on DBT removal at different temperature. The reaction rate constant was estimated through 30 min. Table 5 list the comparison between two kinetic models, since pseudo second order kinetic show the good fit than the pseudo first order kinetics.

Table 5: The Comparison between Kinetics models

Temp. / Order	**25 °C**	
	k	**R^2**
n=1	0.011	0.9653
n=2	5E-6	0.9931
	30 °C	
n=1	0.0122	0.9119
n=2	6E-6	0.9771
	40 °C	
n=1	0.0158	0.7218
n=2	7E-6	0.8935

The activation energy determined from Arrhenius Equation 4, the slope gives the value activation energy 16.724 kJ/mol and the intercept gives the value of pre-exponential factor 4.3678 g/mg. min.

$$\ln k = \ln A - \frac{E}{RT} \qquad \dots (4)$$

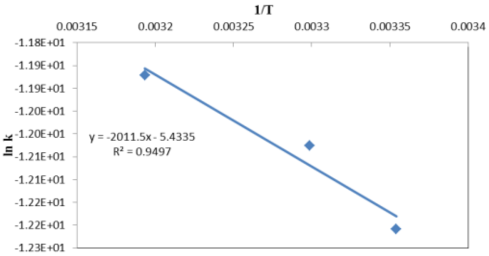


Fig. 10: Rate Constant versus 1/T

5. Pore Diffusion

The effect of internal mass transfer for the ODS of DBT using air and ZnO/AC by calculating the Thiele modulus (M_T) as equation (5) [14].

$$M_T = L\sqrt{\frac{(n+1)K_{eff}C_{OA}^{n-1}}{2D_{eff}}} \qquad \dots (5)$$

For a second order equation the Equation 5 reduced to Equation 6:

$$M_T = L\sqrt{\frac{3K_{eff*}C\ DBT}{2D_{eff}}} \qquad \dots (6)$$

Where the effective diffusivity can be evaluated from Equation 7:

$$D_{eff} = \frac{D_{AB}\epsilon_p}{\tau_p} \qquad \dots (7)$$

In this work, ZnO/AC can be assumed sphere particles, for sphere $L = \frac{R}{3}$, For ZnO/AC, the porosity ε_p are determined as 0.89, while, the tortuosity $\boldsymbol{\tau}_p$ for activated carbon process range 1-12 The value of the tortuosity τ_p can be chosen as 3.5, since many researchers in the literature were chosen this value [15].

The molecular diffusion coefficient of the air in n-nonane is 0.0495 cm^2/s at 67 °C was measured by Cummings 1955 and by extrapolated the value was equal to 0.5789 cm^2/s at 25 °C [16]. The diffusivity change with temperature as shown in Equation 6 [17].

$$D_{AB}/D_{AB0} = (T/T_0)^{3/2} \qquad \dots (8)$$

The calculated Thiele modulus values at different reaction temperature are listed in Table 6. From the results list in Table 6, it can be shown that, all values of Thiele modulus (M_T) are less than 0.4, and this indication that the effect of internal mass transfer on the overall reaction rate can be neglected and these results could be attributed to the small particle size that made pore diffusion resistance very small.

Table 6: Thiele Modulus Calculation

T K	**k g/mg.s**	**D_{AB} cm^2/s**	**$D_{eff.}$ cm^3/cm solid.s**	**M_T**
298.15	8.33E-08	0.05789	0.014721	1.50715E-07
303.15	1.00E-07	0.05936	0.015094	1.55455E-07
313.15	1.17E-07	0.06389	0.016246	1.56958E-07

Conclusion

The oxidation desulfurization can be achieved by using ZnO/AC and air as the oxidant. The optimum conditions for present system by using Tauguchi method are composite loading 2.5 g, 30 °C and 60 min. Percentage Contribution for composite amount is 43.905%, time 34.927% and 21.167% for temperature. Second order kinetics equation can be used to represent the system. The effect of internal mass transfer can be neglected.

Nomenclature

Symbol	**Definition**	**Units**
A	pre-exponential factor	min $^{-1}$
C_0	Initial Dibenzothiophene Concentration	ppm
C_t	Dibenzothiophene Concentration at any time	ppm
D_{eff}	Effective Diffusivity Coefficient	cm^3/cm solid.s
D_{AB}	Molecular Diffusion Coefficient	cm^2/s
E	activation energy of the reaction	kJ/mol
k	Rate Constant of the Reaction	J/mol
K_{eff}	Effective rate constant	g/mg.s
L	characteristic length of the catalyst particles	cm
n	order of the reaction	

Greek Letters

ε_p	Porosity of the catalyst particles
θ	Scattering or Bragg angle
τ_p	Tortuosity of the catalyst pores

Dimensionless Numbers

M_T Thiele modulus

Abbreviations

AC	Activated Carbon
ZnO/AC	Zinc Oxide /Activated Carbon
AFM	Atomic Force Microscope
ASTM	American Standard Test Method
DBT	Dibenzothiophene
BET	Beunauer, Emmett and Teller
ODS	Oxidation Desulfurization
HDS	Hydrodisulfurization
ICDD	International Center for Diffraction Data
MBT	methylbenzothiophene
LGO	light gas oil
RSR	Mercaptan (RSR)
XRF	X- ray Florescence
XRD	X-Ray Diffraction

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