

# Removal of Sulfur (e.g DBT) from Petroleum Distillates using Activated Carbon in a Continuous Packed-bed Adsorption Column

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**Abstract**—In this study, performance evaluation of activated carbon in a continuous packed bed column for the removal of dibenzothiophene (DBT) from petroleum distillates is reported. Model diesel containing only DBT was desulfurized by adsorption using activated carbon as an adsorbent in continuous mode. Scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) was used to check the morphology and elemental compositions of the adsorbent. Surface chemical functionalities were checked using Fourier transform infra-red (FTIR) spectroscopy. The results show that about 16 mg kg<sup>-1</sup> adsorption capacity of the adsorbent for adsorbate at 3 ml min<sup>-1</sup> and adsorbent amount of 2.0 g. In addition, the adsorption behavior of the adsorbent could be perfectly described with Langmuir isotherm model. The kinetics of the adsorption could be described well using Bohart Adams and Thomas models.

**Keywords**- activated carbon, adsorption, dibenzothiophene, diesel, petroleum distillates.

## I. INTRODUCTION

The global demand for energy has increased exponentially over recent years and it is expected to increase by 13.4% between 2013 and 2040. In South Africa for example, fossil fuel energy consumption was reported at 86.91% in 2014 according to the World Bank collection. Of the available energy sources fossil fuels still remains the primary energy resource with a wide possible application [1]. The presence of sulfur compounds in crude oil distillates like diesel is always objectionable due to their process and environmental problems. Sulphur occurs in many forms in crude oil like sulfur, H<sub>2</sub>S, mercaptans, sulfides, disulfide and thiophenes [2].

Diesel amongst others is one of the petroleum-derived fuel which consists of Sulphur [3]. These Sulphur compounds are one of the common impurities present in various petroleum fractions that cause serious health and

environmental problems. The petroleum refining industry perceived as one of the largest sources of pollution, both directly and indirectly via motor exhaust fumes, is on the front line of the battle for realizing environmentally friendly and viable technique [3]. There is a growing pressure on the refineries to produce cleaner petroleum products and to abate or totally eradicate the negative impact on the environment at the same time. Furthermore, sulfur compounds are undesirable in refinery process as they tend to deactivate some catalysts used in crude oil processing and cause corrosion problems in pipeline, pumping and refinery equipment [4]. Moreover, naturally occurring sulfur compounds left in fuel lead to the emission of sulfur oxide gases. The gases react with water into the atmosphere to form sulfates and acid rain which damage buildings, destroy automotive paints furnish and acidifies soil which leads to loss of balanced ecosystems [4]. Sulfur emissions also cause respiratory illness, heart diseases, triggers asthma and contribute to formation of atmospheric particulates, lastly sulfur decrease the diesel engine performance of automobile [5].

However, diesel engine finds widespread application as power source in both mobile and stationary applications [1]. The ubiquity of large diesel engine vehicles in the city environment persuaded regulatory authorities of the need to control the emitted exhaust pollutants [1]. Beginning in 2006 United States Environmental protection agency (EPA), began to phase in more stringent regulations to lower the amount of sulphur in diesel fuel to 15 ppm [1]. The shift from ULSD to deep desulphurization has some technical problems. Some sulfur compounds that have alkyl side chain in the 4 and 6 positions in the dibenzothiophene molecules close to sulphur atom (e.g. 4, 6 dimethyl dibenzothiophene) are difficult to desulfurize under conventional desulphurization conditions [2].

Therefore, the desulfurization of such sulfur species from diesel by hydrodesulphurization (HDS) is a tough challenge. The application of the conventional HDS process on diesel fuel and fuel oil has proven ineffective in attaining the ultra-deep desulphurization and would require catalyst volume of 3 times more [6]. Furthermore, HDS is not effective for removing heterocyclic sulphur compounds such as dibenzothiophene (DBT) [2]. HDS is not cost effective in reducing sulphur content in fuel to 10ppm by using high temperature and pressure, large reactor volume and more active catalyst.

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However, adsorptive desulfurization (ADS) is capable of selectively adsorbing aromatic sulphur compounds from petroleum distillates. Adsorbents such as activated carbon, activated alumina, metal sulphides, zeolite, silica gel, zeolite molecular sieves, carbon molecular sieves, impregnated carbons, clays resins, polymer and carbon nanotubes have been used in desulfurization of petroleum distillates. However, only few of them have shown high selectivity for sulphur compounds such as 4,6 DMDBT, DB and DDBT. In addition, some of these adsorbents have been studied in batch adsorption model.

Although batch adsorption mode is needed for collecting basic data, but continuous adsorption mode is preferable in commercial application [7]. In addition, data obtained from continuous is instrumental to designing an industrial scale desulfurization adsorption column. Furthermore, understanding the adsorption behaviour and kinetics of the activated carbon in a packed-bed column could pave way for the design and optimization. Hence, this study investigated behaviour of the adsorbents during adsorption in a packed-bed column using Langmuir isotherm Bohart-Adam's model and Thomas model for kinetics.

## II. MATERIALS AND METHODS

The adsorbent was Activated Charcoal Norit® activated carbon powder CA 1 from wood was purchased from Sigma – Aldrich South Africa. Model diesel containing only DBT was prepared from Hexane and DBT which were bought from Sigma-Aldrich® South Africa. The model diesel consisted of 0.0625 g in 250 mL of hexane (250 mg/L).

Scanning Electron Microscopy (SEM) was used to check the surface morphology of the activated carbon before and after desulfurization. EDX was used to check the elemental composition of the adsorbent before and after desulfurization.

Desulfurization of diesel fuel was carried out in a custom made adsorption apparatus, (shown in Fig. 1), The set-up has a glass column with an internal diameter of 2.4 cm and bed depth of 20 cm. The activated carbon was packed inside the column and supported with glass beads to enhance flow and reduce pressure drop. The continuous flow experiments were carried out at three different masses, 1.0 g, 1.5 g and 2.0 g of activated carbon while keeping the bed depth at 20 cm. The DBT of the known concentrations 250, 500, 750 and 1000 mg/L was fed into the column in a down-ward flow direction using a peristaltic pump at 3,8 or 10 mL/min. The adsorption time was 1 hr. Samples were withdrawn at regular interval of 15 min for analysis.

The amount of DBT from the samples was measured using a High performance liquid chromatography (HPLC) Eclipse C-18, using acetonitrile (55%) as the mobile phase. Other conditions during the analysis were: Injection Volume 10 µl, Wavelength 234 nm, time taken 10 min, flowrate 10 µl. It is noteworthy to mention that HPLC was calibrated before the analysis. Fig. 1 shows the experimental set-up of the fixed bed column.

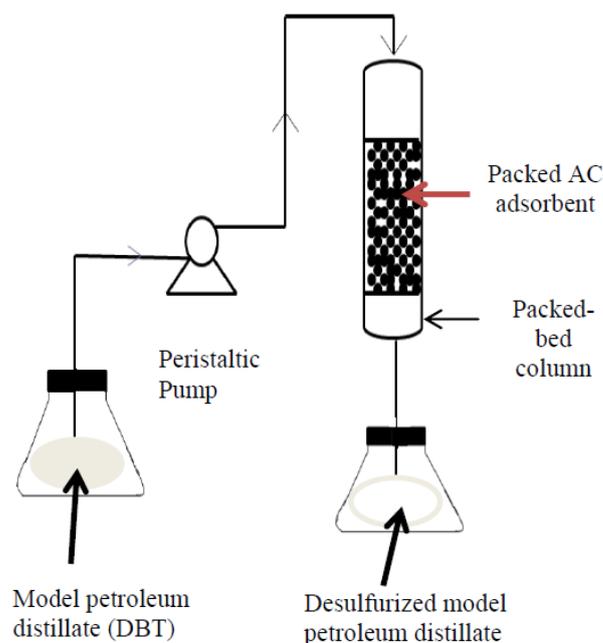


Fig 1: Schematic of the experimental set-up for fixed bed adsorption column

## III. RESULTS AND DISCUSSION

Fig. 2 depicts the SEM images of AC before (Fig. 2a) and after (Fig 2b) adsorptive desulfurization. Generally, the adsorbent with porous and rough morphology has high adsorption capacity (Muzic, 2011). It can be seen from Fig 2(a) and 2 (b) that the difference lies in the roughness and other small particles deposited on the surface of the two. Fig 2a has pore but a bit smoother compared to Fig 2b with pores but rough surface. This could be due to sulfur molecules deposited on the surface of the AC (Muhammad et al. 2015).

Table I shows the elemental compositions of the activated carbon adsorbent before and after desulfurization. Table 1 shows that there was no elemental sulfur on the fresh activated carbon, but 0.26 % of elemental sulfur was observed in used activated carbon after desulfurization. This confirms the adsorption of the DBT on to the surface of the adsorbent after desulfurization.

TABLE I  
 ELEMENTAL COMPOSITIONS OF UNUSED AND USED ACTIVATED CARBON BY EDX

Element	Weight %		Atomic %	
	Fresh Activated carbon	Used activated carbon	Fresh activated carbon	Used activated carbon
C	81.82	84.47	87.07	88.39
O	14.06	14.00	11.23	10.99
P	4.11	0.86	1.70	0.35
S	0.00	0.67	0.00	0.26
Total	100.00	100.00	100.00	100.00

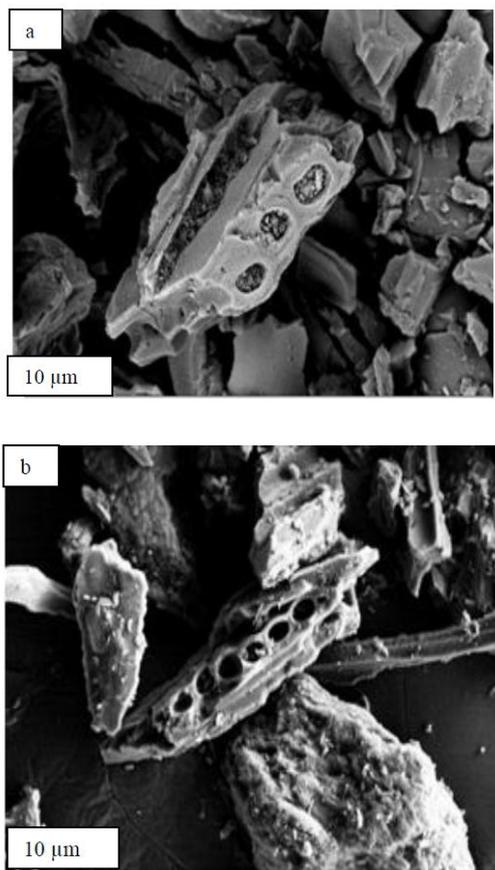


Fig. 2: SEM images of activated carbon before (a) and after (b) desulfurization.

The breakthrough curves at various flow rate 3, 8 and 10 ml min<sup>-1</sup> corresponding to superficial velocities of 0.00898, 0.0239 and 0.0296 m s<sup>-1</sup>, respectively were obtained at the feed concentration of 250 mg L<sup>-1</sup> and adsorbent mass of 2.0 g. From Fig. 3, it is seen that rapid uptake of DBT occurred at the initial stage and the rate decreased thereafter to reach equilibrium at 20 min. The breakthrough generally occurred faster with increase in flow rate. It was observed that breakthrough time decreased with increasing flow rate from 3 mL/min to 10 mL/min. This could be due to the increase in occupancy of the adsorption zone as the feed flow rate increased, which invariably resulted in decrease in time required to attain the specific breakthrough concentration. Flow rate also influence the adsorption of DBT onto activated carbon. As the flow rate increased, the breakthrough curves become steeper and reached the *breakthrough* quickly. The results obtained are in agreement with the work of Music [8] and [9]. At a lower superficial velocity, contact time between the DBT and the AC is increased, thereby resulting in enhanced removal of DBT. This result is similar to what was obtained by other researchers [9]

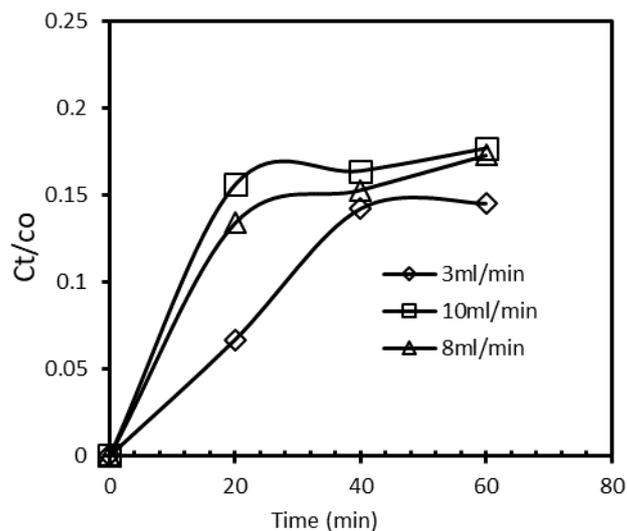


Fig. 3: The effect of flow rate on DBT adsorption. Experimental conditions: DBT concentration: 250 mg/L, Amount of adsorbent: 2.0 g

The breakthrough curves at different amount of AC (1.0, 1.5 and 2.0 g) at feed flow rate of 3 ml L<sup>-1</sup> are shown in Fig.4. It is seen that as the adsorbent mass increases, the breakthrough time also increased. This may be due to increase in number of active binding sites on the surface of the adsorbent in the column which broadens the adsorption transfer zone. Highest DBT removal capacity was observed at the highest adsorbent amount [10]. The adsorbent was quickly saturated at lower adsorbent mass because of the few adsorption sites present for DBT removal [9]. The results are also in agreement with literature [11,12].

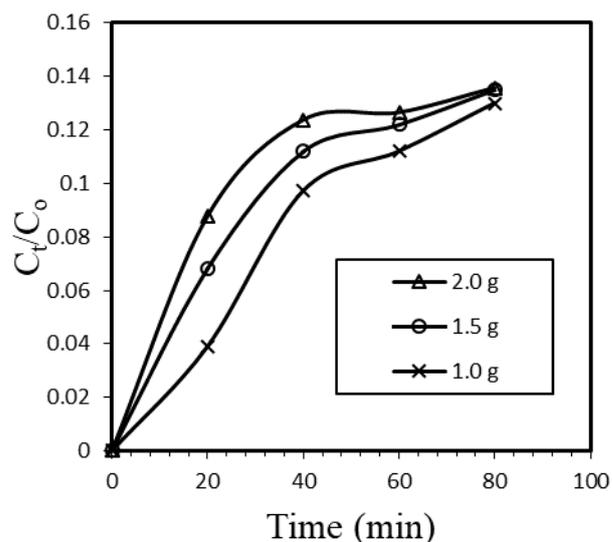


Fig 4: The effect of AC mass on DBT adsorption, Experimental conditions: DBT concentration: 250 mg/L, Feed flow rate: 3 ml/min.

The column data were fitted to the Thomas model (Eq. i) to determine the Thomas rate constant ( $k_{TH}$ ) and maximum solid-phase concentration ( $q_0$ ). The regression coefficients ( $R^2$ ), relative constants were obtained using least square estimation method.

From Table II, it is seen that value of the coefficient of determination ( $R^2$ ) is 0.923. Moreover, as the influent concentration increased the value of  $q_0$  increased and the value of  $k_{TH}$  decreased. The reason is that the driving force for adsorption is the concentration difference between the DBT on the adsorbent and the DBT in the solution. Thus the high driving force due to the higher DBT concentration resulted in better column performance. The result from this study is in agreement with the literature [13].

With flow rate increasing, the values of  $q_0$  decreased and the value of  $k_{TH}$  decreased. As the AC mass increased, the values of  $q_0$  increased and  $k_{TH}$  decreased. So lower flow rate, higher DBT concentration and higher AC mass would increase the adsorption of DBT on the activated carbon column. The similar results were reported by [13] and Muzic et al. [8].

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{TH}q_0Z}{V} - K_{TH}C_0t \quad (i)$$

Where  $q_0$  is the equilibrium DBT uptake per g of the activated carbon (mg/g),  $K_{TH}$  is the Thomas constant (L./min.mg),  $V$  is the flow rate (ml/min),  $Z$  is the height of the bed (cm). A plot of  $\ln\left(\frac{C_0}{C_t} - 1\right)$  against time yields a linear graph. The values of  $K_{TH}$  and  $q_0$  can be calculated from intercept and slope of the graph, using a linear regression analysis.

TABLE II  
ADSORPTION KINETIC PARAMETERS FROM THOMAS MODEL

$C_0$ (mgL <sup>-1</sup> )	Z (cm)	V (mlmin <sup>-1</sup> )	$q_0$ (mgg <sup>-1</sup> )	$K_{TH}$ (mLmg <sup>-1</sup> mL <sup>-1</sup> ) x 10 <sup>-4</sup>	$R^2$	SS
250	2	8	4.5	0.16	1.0	0.45
250	1	3	14	0.44	1.0	0.27
250	2	3	15	2.6	0.99	0.98
500	2	3	33	1.7	0.92	0.28

The Adams–Bohart adsorption model (Eq. ii) was applied to experimental data for the description of the initial part of the breakthrough curve. This approach focused on the estimation of kinetic parameters such as maximum adsorption capacity ( $N_0$ ) and kinetic constant ( $K_{AB}$ ) from the Adams–Bohart model as described Muzic et al. (2008). For all breakthrough curves, respective values of  $N_0$ ,  $K_{AB}$  were calculated and are presented in Table 2, together with the correlation coefficients of regression,  $R^2$  is 0.720 and smaller sum of squares (SS) (less than 0.19).

It can be observed from Table 3 that when initial influent concentration increased, the value of  $N_0$  increased and the value of  $K_{AB}$  decreased. When the flow rate increased, the value of  $N_0$  decreased and the value of  $K_{AB}$  increased. When the mass of adsorbent increased the value of  $N_0$  increased

and the value of  $K_{AB}$  increased. Therefore, it can be concluded that lower flow rate, higher DBT concentration and lower bed height would increase the desulphurization performance of powdered AC in the packed-bed column. In addition, the results showed that the overall kinetics is limited by external mass transfer at the initial stage of the adsorption and these are in agreement with the report of Muzic et al. [8].

$$\ln\left(\frac{C_t}{C_0}\right) = K_{AB}C_0t - \frac{KN_0Z}{V} \quad (ii)$$

Where  $K_{AB}$  is the kinetic constant in L/mg.min,  $V$  is the linear flow rate (mL/min),  $Z$  is the bed height of the column (cm),  $N_0$  is the saturation concentration (mg/L) and  $t$  is time in min. The plot of  $\ln(C_t/C_0)$  versus time yield a linear graph with slope and intercept, from which the Bohart-Adam constants  $K_{AB}$  and  $N_0$  can be calculated, respectively.

TABLE III  
ADSORPTION KINETICS PARAMETERS OF ADAMS-BOHART MODEL

$C_0$ (mgL <sup>-1</sup> )	Z (cm)	V (mlmin <sup>-1</sup> )	$N_0$ (mgL <sup>-1</sup> ) x 10 <sup>-3</sup>	$K_{AB}$ x 10 <sup>-6</sup> (mgmin <sup>-1</sup> )	$R^2$	SS
250	2	8	0.023	6.40	0.72	0.43
250	1	3	0.026	1.04	0.90	0.19
250	2	3	0.110	2.92	0.96	0.66
500	2	3	0.270	1.60	1.00	0.25

Fig 5 depicts the Langmuir isotherm of the adsorption mechanism. The result showed that the adsorption isotherm exhibited a monolayer adsorption mechanism. This is because the amount of DBT adsorbed on to the AC adsorbent increased rapidly with an increase in DBT concentration and then stabilizes afterwards at constant temperature. The Langmuir isotherm has been found to fit well with most liquid/solid adsorption processes and specifically diesel desulphurization processes [14]. Due to its simplicity and ability to well-fit most performances, the Langmuir isotherm has become one of the most popular models in adsorption studies [15]. It was found that Langmuir Isotherm fit well with the experimental data and it is in agreement with Muzic et al. [8]

The Langmuir isotherm equation is represented in Eq. (iii):

$$q_e = \frac{q_m K C_e}{1 + K C_e} \quad (iii)$$

Where  $q_e$  is the amount of DBT adsorbed at equilibrium DBT concentration (ppm),  $q_m$  is the amount of DBT adsorbed with monolayer coverage and  $K$  is the Langmuir constant.

The models both described the kinetics of the adsorption of DBT onto the powdered AC in packed bed column at 500 mg L<sup>-1</sup>, 3 ml min<sup>-1</sup>, 2.0 g. Between the Thomas and Adams-Bohart models, the value of error (SS) for Adams-Bohart was lower for a given experimental condition. Thus, based on the SS values of the two models, it was concluded that

the Adams–Bohart model is better in describing the process of DBT adsorption in powdered Activated carbon column.

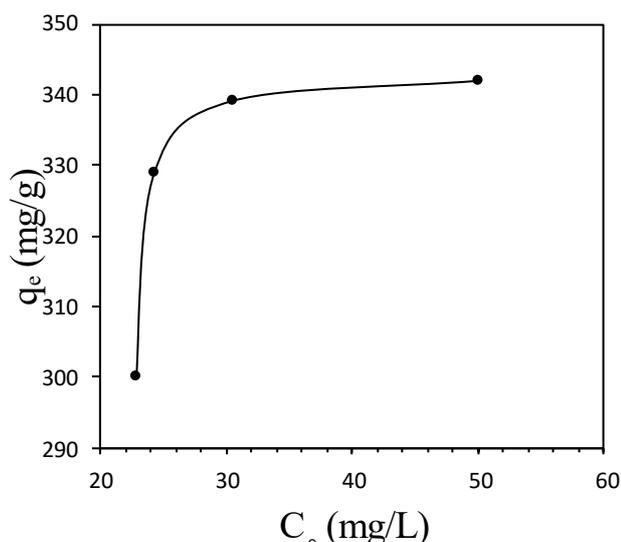


Fig 5: Langmuir Isotherm. Experimental conditions: DBT concentration: 250 mg/L, Flow rate: 3mL/min, Amount of adsorbent: 2.0 g.

#### IV. CONCLUSIONS

Powder activated carbon as an adsorbent has been successfully employed in desulphurization of DBT from model diesel. The adsorption behaviour at constant temperature could be described with Langmuir isotherm. Removal of DBT is influenced by flow rate, DBT concentration in the feed and the amount of adsorbent. The initial region of the breakthrough curve could be described by Bohart-Adam model while the transient stage or working stage of the breakthrough curve could be described by Thomas model. Catalytic modification of the activated carbon could improve its adsorption performance of DBT removal.

#### REFERENCES

[1] J. Eber, P. Wasserstein, A. Jess. Deep desulfurization of oil refinery streams by extraction with ionic liquids. *Green chemistry*, Vol. 6, No. 7, pp.316-322, 2004.

[2] F. Senyangane, Simulation of the adsorption Desulphurization of Diesel fuel. MSc. Wits University. 2016.

[3] S. A. Alavi, S. R. Hashemi. A Review on Diesel Fuel Desulfurization by Adsorption Process. *International Conference on Chemical, Agricultural, and Biological Sciences (ICCABS'2014)*, pp. 9-10, 2014.

[4] P. Gawan, J. Kaware. Desulphurization techniques for liquid fuel A Review. *International of Engineering Technology Management and applied Science*. Vol. 2, No. 7, pp. 122-126, 2014.

[5] Y. C. Bhattachryulu, M. Patil, S. Kamble, Unsteady state adsorption – Column studies. *International Journal of Advanced Engineering Research and Studies*, Vol. 1, No. II, pp. 179– 184, 2012.

[6] P. Gawan, J. Kaware. Review of Research for

Desulphurization of diesel by Adsorption. *Journal of Engineering and Technology International Research*. Vol. 3, No. 12, pp. 337-340. 2016.

[7] P. Gawan, J. Kaware Review on low cost Adsorbents for Desulphurization of Liquid Fuels. *International Research Journal of Engineering and Technology*. Vol. 2, (1), pp. 108-112, 2016.

[8] H. E. Muftah, A. A. Manal, A. Sulaiman, Evaluation of an activated carbon packed bed for the adsorption of phenols from petroleum refinery wastewater. *Environ Sci Pollut Res*, Vol. 24, pp. 7511–7520, 2017.

[9] M. Muzic, B. Sertic, T. Adzamic, Z. Gomzi, S. Podolski. Optimization of diesel fuel desulfurization by adsorption on activated carbon, *Chem. Eng. Trans.*, Vol. 17, No. 5, pp. 1549-1554, 2009.

[10] M. Muzic, S. Katica, A. Tamara.” Kinetic Equilibrium and statistical analysis of diesel fuel adsorptive desulphurization” Vol. 4, No. 9, pp. 373-394, 2009.

[11] Neran, K., Ibrahim, A., Samar, K., Aljanabi, S. “Desulfurization and Kinetic Study of Diesel Fuel by Batch Adsorption on Activated Carbon”, *Eng. & Tech. Journal*, Vol. 7, No. 33, pp. 1901-1916, 2015.

[12] J. Ahmed, M. Ahmaruzzaman.). “Adsorptive desulfurization of feed diesel using chemically impregnated coconut coir waste” *Int. J. Environ. Sci. Technol*. Vol. 2, No. 9, pp. 2847–2856, 2015

[13] K. Tang, L. Song, L. Duan, X. Li, J. Gui, Z. Sun, “Deep desulfurization by selective adsorption on a heteroatoms zeolite prepared by secondary synthesis. *Mater*. Vol. 145, pp. 331–335, 2008

[14] R. Han, W. Yu, Z. Xin, W. Yuan, X. Fuling J. Cheng, M. Tang. “Adsorption of Methyl Blue by Phox Tree Leaf Power in a Fixed Bed Column: Experiments and Prediction of Breakthrough Curves. *Desalination*. Vol. 2, No. 45, pp. 284-297, 2009.

[15] H. Rang, J. Kan, V. Oja. ‘Advances in desulfurization research of liquid fuel’, *Oil Shale*, Vol. 23, No. 2, pp. 164-176, 2006.

[16] A. Sam, N. Noora, S. Yehya, S. Zarook, S. Ziad “Adsorptive Desulfurization of Commercial Diesel oil Using Granular Activated Charcoal” *Int’l Journal of Advances in Chemical Engineering., & Biological Sciences (IJACEBS)*. Vol. 2, (1), pp. 15-18, 2015.