



# Adsorptive desulphurization study of liquid fuels using Tin (Sn) impregnated activated charcoal



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## HIGHLIGHTS

- Tin impregnated activated charcoal (Sn-AC) was used as an adsorbent for dibenzothiophene (DBT) removal from model and real oil samples.
- Maximum DBT removal was achieved from model oil at optimized conditions of temperature 60 °C, stirring time 1 h and adsorbent dosage 0.8 g.
- The spent adsorbent was regenerated with toluene washing and was used for DBT adsorption for multiple folds.
- Sn-AC was then used for the desulphurization of commercial kerosene and diesel oil samples.

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## ABSTRACT

Keeping in view the growing concern regarding desulphurization of petroleum products, the present study was under taken to investigate the efficiency of tin impregnated activated charcoal (Sn-AC) as a potential adsorbent for the desulphurization of model and real commercial straight run kerosene and diesel oil samples. The adsorbent Sn-AC was prepared by wet impregnation process in the laboratory and characterized by SEM, EDX and surface area analysis. Initial experiments were carried out using model oil, which was prepared by dissolving dibenzothiophene (DBT) in cyclohexane, the optimum conditions for desulfurization were found to be, 60 °C temperature, 1 h contact time and adsorbent dosage of 0.8 g, under which about 99.4% of DBT removal was attained. Under optimized conditions the desulfurization of real oil i.e., kerosene and diesel oil was also investigated. Kinetic studies revealed that DBT adsorption followed pseudo second order kinetics and the data best fits in the Langmuir adsorption isotherm as compared to Freundlich adsorption isotherm model. The adsorbent could be easily regenerated simply by washing with toluene for a multiple cycles and reused without losing its efficiency.

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## 1. Introduction

Compounds of sulfur (S) in the transportation fuels have remained as the major culprits, responsible for the environmental pollution by producing the noxious oxides of sulfur (SO<sub>x</sub>) during combustion. In order to minimize such pollution, increasingly stringent regulations are being imposed to reduce the S-content to a very low level, such as 10–20 ppm in the transportation fuels [1].

Dibenzothiophene (DBTs) and its derivatives present in fuel oils such as kerosene and diesel oil are considered to be refractory poly-aromatic sulfur compounds. Particularly, alkyl-substituted DBTs, i.e., 4-methyldibenzothiophene (4-MDBT) and

4,6-dimethyldibenzothiophene (4,6-DMDBT), are highly refractory [2]. Adsorption is one of the desulfurization tools which hold promise to efficiently remove these refractory sulfur compounds under low cost. Recent research studies reveal that reactive adsorption is superior to ordinary physical adsorption, because it involves  $\pi$  complexation between aromatic sulfur compounds and the adsorbent, which is stronger than van der Waals interaction. However  $\pi$ -complexation can be broken easily by heating or decreasing pressure, thereby it is easy to regenerate the adsorbent [3].

Different metal cations impregnated on various supports have been used as reactive adsorbents for the desulfurization of liquid fuels. Hernández-Maldonado et al. investigated the removal of thiophene from the simulated feedstock using Cu(I)-Y and Ag-Y zeolites [3]. McKinley et al. employed Ag-I/SBA-15 and Ag-I/SiO<sub>2</sub> as adsorbents for the selective removal of DBT and 4,6-DMDBT from Model oil [4]. Metals halides, CuCl<sub>2</sub> and PdCl<sub>2</sub> supported on activated

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carbon have also been found to be effective for desulfurization of jet fuel [5,6].

Nowadays activated carbon (AC) is extensively used as adsorbents because of its well-developed porosity, high specific surface area and tunable surface oxygen-containing complexes. An attractive way for adsorptive desulfurization, porous materials can be used for acquiring ultra-deep desulfurization of distillate fuels. Activated carbons (ACs), activated carbon fibers and catalyst-loaded ACs have been considered as the most efficient materials for adsorptive desulfurization [7]. Modification of AC by concentrated  $H_2SO_4$  at  $250^\circ C$  has shown greater adsorption capacity for DBT than the unmodified AC [8].

In the current study, the adsorption of DBT from the model as well as real commercial kerosene and diesel fuel oils was performed using low cost whole and chemically modified adsorbents. The effect of different adsorption parameters i.e., amount of the adsorbent, temperature, and the contact time were studied to get optimum desulfurization of the samples under study.

## 2. Experimental

### 2.1. Samples collection

Straight run kerosene and diesel oil samples were collected from Attock Oil Refinery, MORGAH, Rawalpindi, Punjab, Pakistan. The samples were used as such without further pretreatment.

### 2.2. Model oil (MO) preparation

Dibenzothiophene (DBT) and cyclohexane (99%) were purchased from Sigma Aldrich. The reagents were of analytical grade and were used without further purification. For preparation of MO stock solution, 1 g of (DBT) was dissolved in 1 L of cyclohexane to make 1000 ppm DBT solution. Different standard DBT solutions were prepared and analyzed using UV–vis double beam spectrophotometer. Fig. 1 shows the calibration curve for standard DBT solutions at  $\lambda_{max}$  320 nm [9].

### 2.3. Activated charcoal (AC)

Granular AC was procured from Sigma–Aldrich. It was crushed and ground using mechanical crusher/grinder and sieved through  $180 \mu m$  screen. The powdered AC was stored in an air tight bottle for further treatment.

#### 2.3.1. Tin (Sn) impregnated AC

$SnCl_2$  salt solution was used as metal precursor and 10 wt% of Sn was loaded on powdered AC using wet impregnation technique.

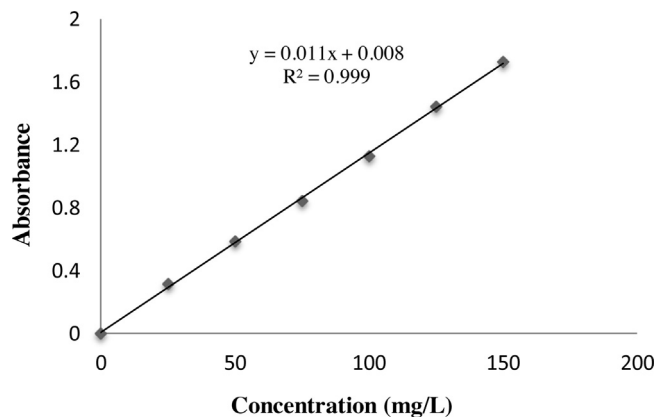


Fig. 1. Calibration curve for the determination of DBT concentrations.

A stoichiometric amount of powdered AC was added to the corresponding metal salt solution and was heated up to  $60^\circ C$  for one hour with constant stirring. It was dried in an oven below  $100^\circ C$ . After complete drying, the adsorbent was stored in an air tight glass vial for further use.

### 2.4. Desulphurization study

In a typical desulphurization experiment, 15 mL of sample oil was taken in a 100 mL round bottom flask and a known amount of adsorbent was added to it, the flask was connected to a reflux condenser and mounted on heating bath. The mixture was heated up to  $60^\circ C$  with constant stirring for a known duration. It was then filtered using Wattman filter # 42. The filtrate collected was then analyzed for the residual DBT using standard calibration curve method.

#### 2.4.1. Model oil desulphurization

To get the maximum DBT adsorption, the desulphurization of model oil was studied under different adsorption conditions including adsorbent dose, temperature and contact time. For the optimization of one parameter, the other two parameters were kept constant, varying only that parameter which was to be optimized. The amount of DBT adsorbed in percent (% adsorption) and milligram per gram adsorbent (mg/g) was also calculated by the following relations:

$$\text{DBT\% adsorption} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

$$\text{DBT adsorption} \left( \frac{\text{mg}}{\text{g}} \right) = \frac{(C_i - C_e)}{W} \times V \quad (2)$$

where,

“ $C_i$ ” is the initial DBT concentration before adsorption.

“ $C_e$ ” is the equilibrium concentration of DBT after adsorption.

“ $W$ ” is the amount of adsorbent used.

“ $V$ ” is volume of the model oil taken.

#### 2.4.2. Desulphurization of real fuels/commercial samples

Desulphurization study of the real samples was also carried out under the same set of experimental conditions as afore mentioned.

### 2.5. Regeneration of spent adsorbents

The spent adsorbents were regenerated by washing with a number of solvents including methanol, acetonitrile, chloroform and toluene. However, toluene showed best results in the regeneration of spent adsorbent up to five fold. For every successful regeneration cycle, about 5 mL of toluene per gram of adsorbent was used. The regenerated adsorbent was filtered and dried in an oven below  $100^\circ C$  for one hour, which was reused.

### 2.6. Analyses

#### 2.6.1. Characterization of kerosene and diesel oil samples

Various physicochemical properties of kerosene and diesel fuel were examined by following the ASTM and IP standard methods like; Conradson carbon residue (ASTM D 189-01/IP 13/92), Ash content (ASTM D 482-03/IP 4/81), Kinematic viscosity (ASTM D 445-04/IP 71/87), Aniline point (ASTM D 611- 04/IP 2/78), Pour point (ASTM D 97- 05/IP 15/67), Flash point (ASTM D 56-05/IP 34/87), Specific gravity (IP 160/87), Elemental analysis (sulfur analysis), Sulfur analysis (Eschka mixture method) (ASTM D3177-89), Sulfur analysis (Bomb washing method) (ASTM D 129-83/IP 61/84) [10].

### 2.6.2. Characterization of the adsorbent

The adsorbent samples were characterized by SEM, EDX and surface area analysis. Detailed procedures are given as under.

**2.6.2.1. Scanning electron microscopy (SEM).** The texture and morphology of the different adsorbents including virgin, modified and treated samples after desulphurization was examined by scanning electron microscope Model No. JEOL-Jsm-5910; Japan.

**2.6.2.2. Energy dispersive X-rays (EDX) analysis.** The mineralogical composition of the different adsorbents used in the adsorption study was examined by Energy Dispersive X-rays Spectrometer (EDX Model Inea 200, UK Company Oxford).

**2.6.2.3. Surface area analysis (SAA).** BET surface area ( $S_{BET}$ ), BJH surface area ( $S_{BJH}$ ), average pore size and average pore volume was determined from nitrogen isotherms at 77.4K using surface area and pore size analyzer (NOVA 1200e). Prior to each measurement, the sample was degassed to  $10^{-4}$  Torr at 100 °C for 2 h.

### 2.6.3. Instrumental analysis of oil samples

The compounds of sulfur present in kerosene and diesel oil samples were detected quantitatively using a variety of techniques.

**2.6.3.1. Sulfur analysis by leco carbon-sulfur analyzer.** Total sulfur in the straight run and treated kerosene and diesel oil samples was analyzed by computer software controlled Leco SC-144DR carbon sulfur analyzer.

**2.6.3.2. UV spectroscopy.** The virgin and treated model oil was analyzed using a double beam UV–vis spectrophotometer [Shimadzu 160 A, Japan]. The spectrum was recorded between the ranges of 200–400 nm wavelength. DBT gave its maximum absorbance ( $\lambda_{max}$ ) at 320 nm as reported earlier [9]. Pure cyclohexane was used as a reference solvent.

From the model oil (1000 ppm DBT in cyclohexane), a series of standard solutions were prepared by diluting it in cyclohexane by simple dilution method. The absorbance of each standard solution was measured at 320 nm wavelength using UV–vis spectrophotometer. From the absorbance data of the standard DBT solutions, a calibration curve was constructed which gave a straight line as shown in Fig 1. The DBT concentration of unknown solution left after adsorption was determined by the calibration curve's straight line equation.

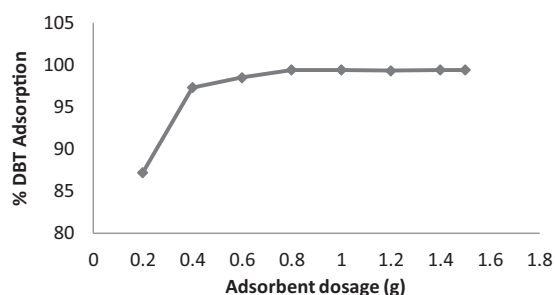
## 3. Results and discussion

### 3.1. Characterization of kerosene and diesel oil samples

Various physico-chemical properties of kerosene and diesel samples were determined, results are provided in the Table 1, which shows that the samples meets the standard kerosene and

**Table 1**  
Physico-chemical characteristics of kerosene and diesel oil samples.

| S. no. | Characteristics                    | Kerosene | Diesel |
|--------|------------------------------------|----------|--------|
| 1      | Specific gravity at 15 °C (60 °F)  | 0.803    | 0.841  |
| 2      | Density (g/cm <sup>3</sup> )       | 0.764    | 0.837  |
| 3      | API gravity                        | 44.71    | 41.03  |
| 4      | Kinematic Viscosity (Cst) @ 100 °F | 2.32     | 3.64   |
| 5      | Aniline Point °C                   | 56       | 64     |
| 6      | Flash Point °C                     | 47       | 53     |
| 7      | Pour Point °C                      | 12       | 09     |
| 8      | Conradson Carbon Residue (wt%)     | 0.21     | 0.23   |
| 9      | Ash content (wt%)                  | 0.04     | 0.06   |
| 10     | Total Sulfur (wt%)                 | 1.352    | 1.871  |



**Fig. 2.** % DBT adsorption a function of adsorbent dose using Sn-AC as adsorbent.

diesel fuel specifications [11,12]. The focus of the present study was on the removal of the sulfur content. Sulfur contents increases as the boiling range of the petroleum fractions increases. As sulfur compounds exist in different forms at different boiling range. The sulfur content detected in commercial kerosene and diesel samples are provided in the table, which indicate that both the oils have high total sulfur content exceeding the amount of 1%. So, it must be subjected to desulphurization prior to be sent out to the market.

### 3.2. Effect of metal impregnation on DBT adsorption

Based on the results, compared to raw/virgin AC, tin (Sn) impregnated AC showed the higher DBT adsorption. Due to the  $\text{Sn}^{+2}$  ions impregnation on the surfaces of the AC, it resulted in the variation of activation energy of the DBT adsorption, which could be ascribed to the variation of the local hardness of the AC surfaces [13]. In this case, the SHAB principle, which was proposed by Pearson, can be used to explain the effects of the local hardness of the AC surfaces on adsorption of DBT [14–16]. The adsorption property of an adsorbent not only was determined by its porous micro texture but was also found to be strongly influenced by the chemical property of its surface.

The SHAB principle was locally applied: “hard regions of a system prefer to interact with hard reagents whereas soft regions prefer soft species”. To make a quantitative treatment of hardness, Parr and Pearson used the density functional theory (DFT). The absolute hardness of DBT was found to be 5.267 and its electronegativity was calculated as 2.673. In terms of Pearson hard–soft base classification, DBT was considered as a soft base due to its absolute electronegativity less than 2.8.

According to Pearson classification, the ions  $\text{Sn}^{+2}$  belonged to Block A borderline acids. When different metal ions were separately loaded onto AC by surface impregnation method, the surface local hardness of the AC could be changed. The loading of borderline acid ions  $\text{Sn}^{+2}$  led to the increase in the local soft acid of the AC surfaces [13].

According to a simple rule of the hard and soft acids and bases (SHAB) principle that hard acids prefer to bond to hard bases, and soft acids prefer to bond to soft bases, it can be predicted that the loading of  $\text{Sn}^{+2}$  might have enhanced the interaction between DBT and the  $\text{Sn(II)/AC}$  surfaces because  $\text{Sn}^{+2}$  is a soft acid and DBT was soft base [17]. In addition, it can be also predicted that the loading of  $\text{Fe}^{3+}$  may possibly weaken the interaction between DBT and the  $\text{Fe(III)/AC}$  surfaces because  $\text{Fe}^{3+}$  belong to Block B transition metal and acted as hard acid, while DBT was soft base [17,18].

The effect of various adsorption parameters including adsorbent dose, temperature, and contact time on Sn-AC was studied. The adsorbate dose of DBT (1000 ppm), the stirring speed (100 rpm), and the pH (neutral) were kept constant as reported in the literature [7,9,19]. The residual samples were analyzed for sulfur contents to

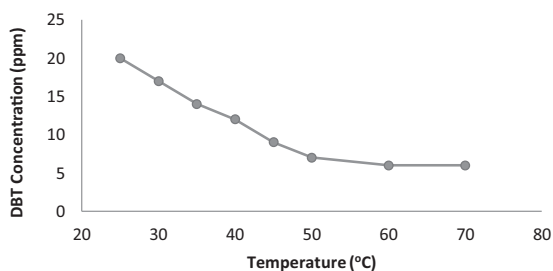


Fig. 3. % DBT adsorption as a function of temperature.

calculate the change in concentration. The results are provided in the proceeding sections.

### 3.3. Effect of adsorbent dosage

The rate of adsorption was studied with various adsorbent doses (0.2–1.5 g/15 mL). The results are provided in Fig. 2. Various reaction conditions such as temperature at 60 °C, stirring speed of 100 rpm, contact time of 1 h and initial DBT concentration 1000 ppm were kept constant.

The results indicated that the DBT removal from model oil was sharply increased from 87.2% to 99.4% (residual DBT amount, 6 ppm) with the amount of adsorbent ranging from 0.2 to 0.8 g and no further increase was observed when the adsorbent dose was increased from 0.8 g to 1.5 g. Finally, 0.8 g of Sn–AC adsorbent dose was chosen as an optimum amount to achieve deep desulfurization of the samples under study.

### 3.4. Effect of temperature

In order to investigate the effect of temperature, the model adsorption experiments were carried out under different temperatures i.e., 25, 30, 35, 40, 45, 50, 60, 65 and 70 °C (Fig. 3). In all the experiments the stirring speed was 100 rpm, adsorbent dosage 0.8 g and initial DBT concentration was 1000 ppm.

At 25 °C, the adsorption percentage was 98 and at 60 °C it was increased to 99.4%. It was obvious that the removal of DBT increased as the temperature increases.

On the other hand, it could be found that DBT was almost completely eliminated at 60 °C and no further DBT adsorption was observed beyond this temperature. In view of economizing the energy, DBT adsorption at 60 °C was chosen as an optimal condition for the desulfurization process using Sn–AC as an adsorbent.

It was observed that as the temperature was increased, the rate of adsorption was also increased, which is due to the increase in

Table 2

Comparison of kinetic parameters of DBT adsorption on Sn–AC.

| Pseudo 1st order equation parameters |        | Pseudo 2nd order equation parameters   |      |
|--------------------------------------|--------|--|------|
| $K_1$ ( $\text{min}^{-1}$ )          | 0.0345 | $K_2$ ( $\text{mg/g}\cdot\text{min}$ ) | 0.32 |
| $q_e$ ( $\text{mg/g}$ )              | 25.94  | $q_e$ ( $\text{mg/g}$ )                | 25   |
| $R^2$                                | 0.998  | $R^2$                                  | 1    |

kinetic energy of sorbent particles and also due to the bond breakage between various functional groups on the sorbent surface and appearance of new functional groups, which may also increases the rate of adsorption with elevation in temperature. From the compiled results, it can be indicated that the adsorption process is endothermic in nature at the given temperatures as reported earlier [20].

### 3.5. Kinetics study of DBT adsorption/Effect of contact time

For the determination of kinetic parameters, the adsorption study was conducted at four different contact time i.e., 15, 30, 45 and 60 min. Optimum reaction conditions such as amount of adsorbent dose (0.8 g) and reaction temperature of 60 °C were applied. The stirring speed was kept constant at 100 rpm, initial DBT concentration of 1000 ppm and at neutral pH. It was observed that with the increase of contact time, DBT adsorption was linearly increased till it reaches to almost 100% at a contact time of 60 min, so no further studies were conducted beyond 60 min as the given target was already achieved. Based on the results of this study, contact time of 60 min was chosen as the optimum reaction time for the complete removal of DBT from the model oil.

The adsorption mechanism was elucidated using two kinetic models i.e., pseudo first order and pseudo second order equations. Both the models were applied to the given data as shown in the Fig. 4(a & b), respectively.

By plotting  $\ln(q_e - q_t)$  against time “ $t$ ” for the pseudo first order equation and plotting “ $t/q_t$ ” against time “ $t$ ”, gave a straight line with slope and intercept. From the given straight line equations, the values for  $q_e$ ,  $K_1$  and  $K_2$  were calculated which are presented in the Table 2. From the “ $R^2$ ” value it can be deduced that the given data best follows pseudo second order kinetic model. The experimental value for the amount of adsorbate adsorbed at equilibrium “ $q_e$ ” was 24.85 mg/g compared to calculated value of 25 mg/g which is almost equal to the experimental value.

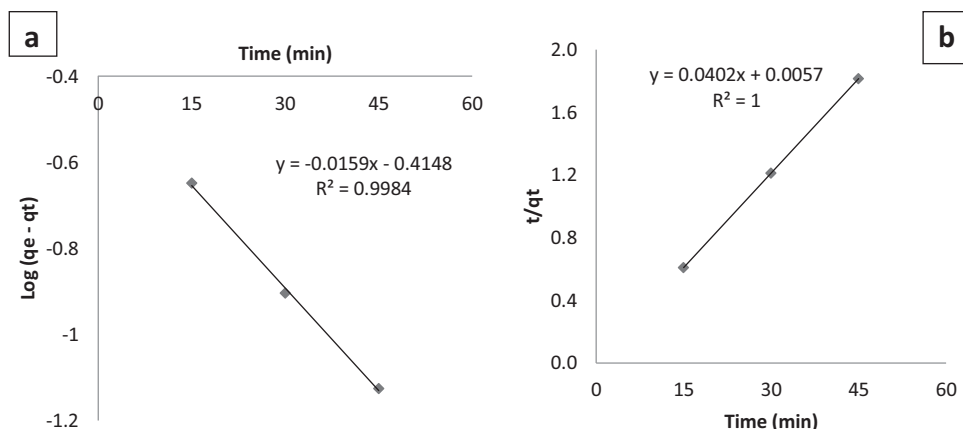


Fig. 4. Pseudo 1st (a) and (b) pseudo 2nd order kinetics determination.

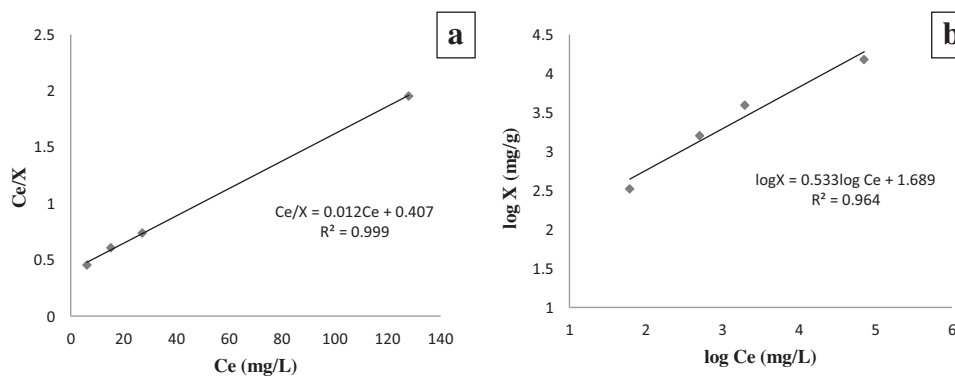


Fig. 5. Adsorption isotherms, (a) Langmuir, (b) Freundlich Adsorption models.

### 3.6. Adsorption isotherms for DBT adsorption on Sn-AC

Many Adsorption isotherms have been used to interpret the experimental data. The two commonly applicable are the Langmuir and Freundlich isotherm model.

The Langmuir adsorption model suggests monolayer coverage on homogenous surface of the adsorbent [21] which can be given simply by the following relation:

$$\frac{C_e}{X_e} = \frac{1}{K_1 q_m q_m} + 1 C_e \quad (3)$$

where “ $C_e$ ” is the DBT equilibrium concentration in the solution (mg/L), “ $X_e$ ” is the amount of DBT adsorbed at equilibrium, “ $K_1$ ” is the Langmuir constant and  $q_m$  is the total amount of the DBT required for complete monolayer coverage (mg/g).

The Freundlich adsorption isotherm model suggests a multilayer adsorption with a heterogeneous distribution of the functional groups, accompanied interaction among the adsorbed molecules [21]. The Freundlich isotherm model can be shown in the given relation:

$$\log X_e = \log K_f + \frac{1}{n} \log C_e$$

where “ $X_e$ ” is the amount of DBT adsorbed at equilibrium (mg/g), “ $K_f$ ” is the Freundlich constant, “ $C_e$ ” is the equilibrium concentration of DBT in the solution (mg/L) and “ $n$ ” is the adsorption intensity.

The Langmuir isotherm model for Sn-AC adsorbent (Fig. 5a) is shown by the linear plot of “ $C_e/X$ ” versus “ $C_e$ ”. The values of “ $q_m$ ” and “ $K_1$ ” were calculated as presented in the Table 3. The Freundlich isotherm model (Fig. 5b) is shown by the linear plot of “ $\log X_e$ ” versus “ $\log C_e$ ”. The values of “ $n$ ” and “ $k_f$ ” were calculated by the slope and intercept, which are presented in the Table 3.

Table 3

Langmuir and Freundlich equation parameters with corresponding correlation coefficients.

| Langmuir isotherm parameters | Freundlich isotherm parameters |       |       |
|------------------------------|--------------------------------|-------|-------|
| $q_m$ (mg/g)                 | 82.64                          | $n$   | 1.876 |
| $K_1$                        | 0.0297                         | $K_f$ | 0.227 |
| $R^2$                        | 0.999                          | $R^2$ | 0.964 |

From the coefficients of correlations ( $R^2 = 0.999$  for Langmuir and  $R^2 = 0.964$  for Freundlich), It is clear that the Langmuir adsorption isotherms coincide well with the experimental data, indicating that the adsorption of DBT on Sn-AC can be well expressed by the Langmuir adsorption isotherm [22].

The applicability of Langmuir isotherm model suggests that the adsorption takes place on homogeneous sites that are identical and energetically equivalent [21].

### 3.7. SEM analysis of original and spent Sn-AC

SEM micrographs of Sn-AC (before and after DBT adsorption) are displayed in the Fig. 6(a & b) respectively. The micrograph of Sn-AC before adsorption clearly shows the porous surface with white spots of uniformly dispersed tin (Sn) on its surface. Major fissures and channels of mesoporous and microporous nature are evident. However, in case of DBT treated Sn-AC, the porosity is fairly decreased due to the imbibition of DBT molecule in micro and mesopores, however, some mesopores are still present. White spots are also absent which is due to more specific interactions, including soft acid-base and  $\pi$ -complexation between DBT molecules and  $Sn^{+2}$  on the adsorbent surface [23].

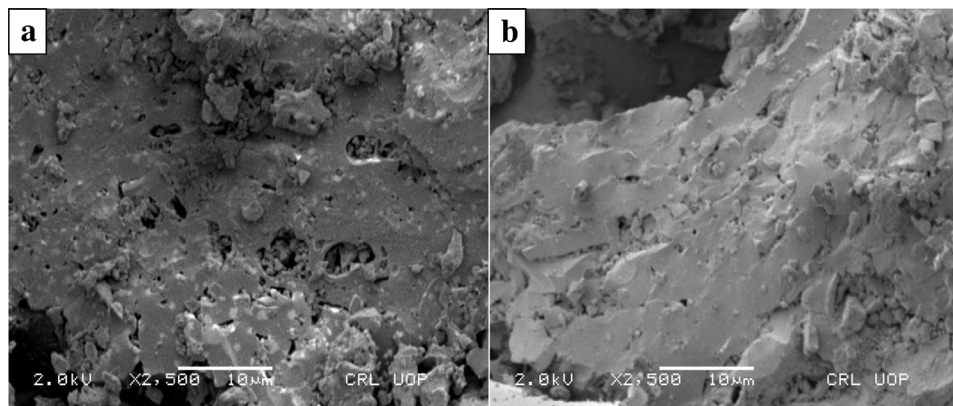


Fig. 6. SEM image of Sn-AC (a) before and (b) after DBT adsorption.

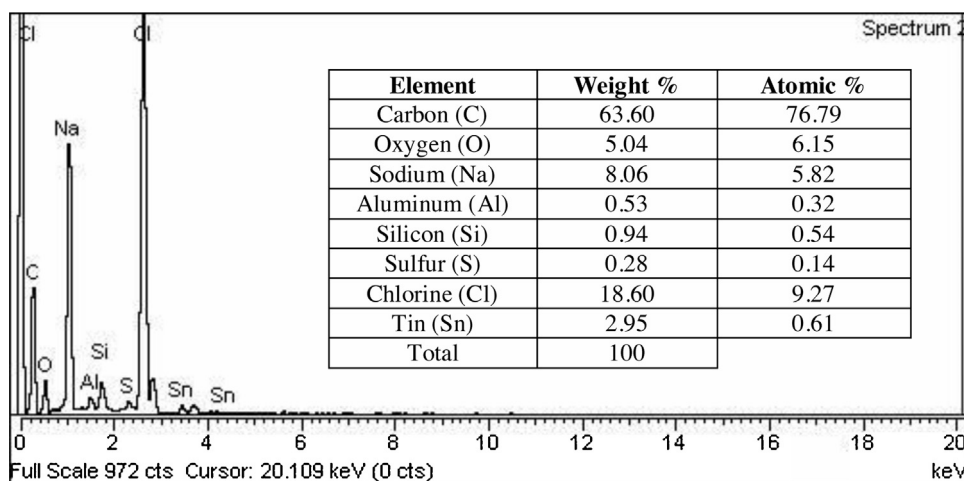


Fig. 7. EDX spectrum of Sn-AC before DBT adsorption.

### 3.8. Surface area analysis of Sn impregnated AC

BET surface area  $S_{BET}$ , BJH surface area  $S_{BJH}$ , average pore volume and average pore diameter was determined for tin impregnated AC.

Compared to raw/virgin AC, Sn-AC modified AC showed 3.45% increase in BET surface area ( $S_{BET} = 83.29 \text{ m}^2/\text{g}$ ), 37.98% increase in BJH surface area ( $S_{BJH} = 81.29$ ), 16.66% increase in average pore volume (0.06 cc/g) having average pore diameter of 31.73 Å.

### 3.9. Energy dispersive X-rays (EDX) analysis

The mineralogical composition of the adsorbents used in the adsorption study was examined by Energy Dispersive X-rays Spectrometer (EDX Model Inea 200, UK Company Oxford).

The EDX profile of Sn-AC is shown in the Fig. 7. It is clear that the adsorbent mostly consists of carbon, oxygen, sodium, aluminum, silicon, sulfur, chlorine and tin.

$\text{SnCl}_2$  was used as Sn metal precursor. The EDX spectrum shows the appearance of Sn metal round about 3 weight percent.

### 3.10. Comparison of original and spent adsorbents

#### 3.10.1. Real commercial oil desulphurization with Sn-AC

After optimization of reaction conditions using model fuel, the same set of optimized reaction conditions were applied for the desulphurization of real fuels. The results for kerosene and diesel oil samples percent desulphurization using different adsorbents are shown in Fig. 8. In comparison to raw/virgin AC, the modified AC showed a remarked increase in the percent desulphurization of kerosene and diesel oil samples. Sn-AC attained a maximum percent adsorption in both kerosene and diesel oil samples with 80.69% in kerosene and 72.10% in case of diesel oil. However, the percent desulphurization for real fuels

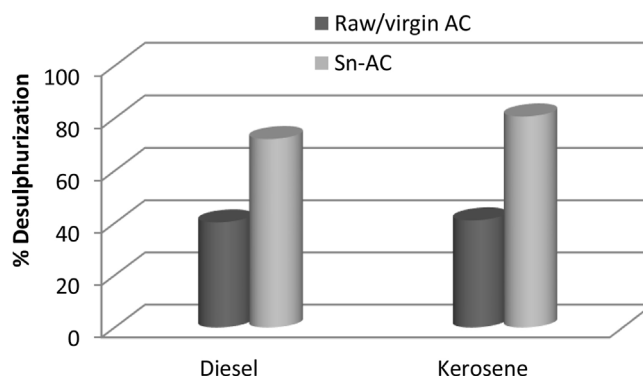


Fig. 8. Percent desulphurization of kerosene and Diesel oil samples with Sn-AC.

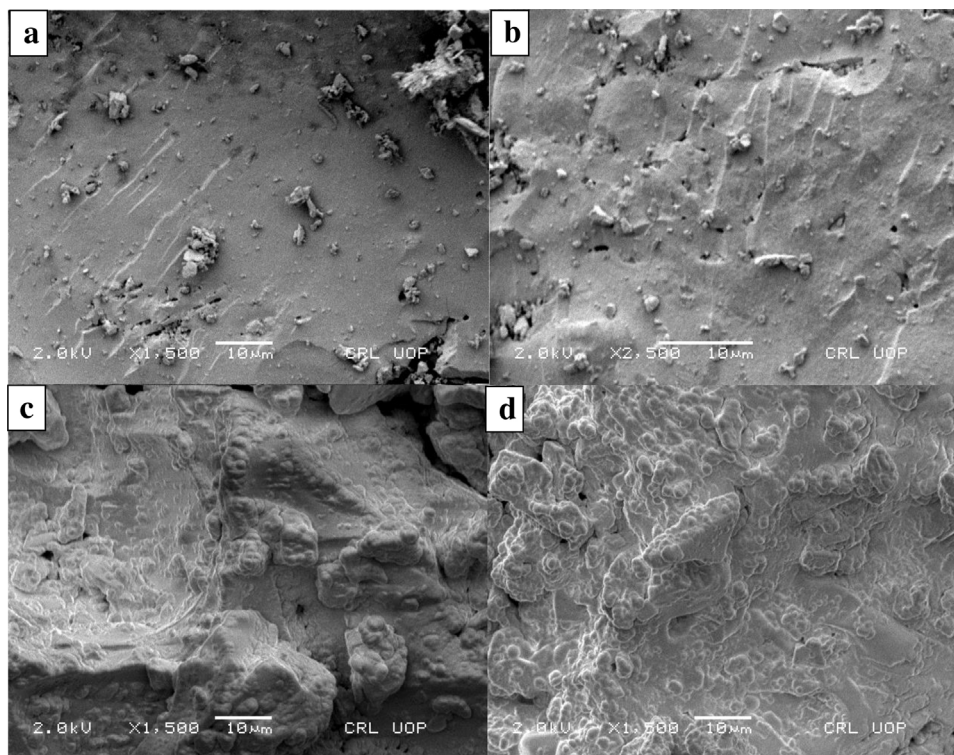
was less than that of model fuel. It may be just because of the presence of several type of aromatic sulfur species in real fuels including BT, DBT, 4-MDBT, 2-MDBT, 4,6-DMDBT, 2,8 or 2,4-DMDBT, 2,4,6-Tri-MDBT, 2,4,8-Tri-MDBT, 2,4,6,8-Tetra-MDBT and 8,9,10,11-Tetrahydrobenzo-[b]naphtho[2,1-d]thiophene. As the number of methyl groups on thiophenic compound increases, the steric hindrance also increases due to which the possibility of sulfur removal is decreased. Moreover, light aromatic sulfur species like BTs, DBTs and MDBTs are adsorbed rapidly on the adsorbent surface which blocks the active sites on the adsorbent surface for the upcoming bulky aromatic sulfur species [24].

SEM micrographs after the desulphurization of commercial kerosene and diesel oil clearly shows that the micro and mesoposity is completely absent in the case of diesel oil treatment i.e., all the pores are completely disappeared and blind leaving behind a bulky masses on the adsorbent surface, however some micropores are visible in the case of kerosene treated adsorbents. It is simply because of the more viscous nature of diesel oil and also more bulky

Table 4

Comparison of the% removal of DBT from liquid fuels by various adsorbents.

| Solvent           | Adsorbent                | % Removal | Ref.         | Perpetration method                      |
|-------------------|--------------------------|-----------|--------------|--|
| <i>n</i> -decane  | Granular activate carbon | 90        | [25]         | Chemical activation with $\text{ZnCl}_2$ |
| <i>n</i> -decane  | Activated carbon fiber   | 45        | [26]         | Commercial                               |
| <i>n</i> -hexane  | Activate alumina         | 60        | [20]         | Commercial                               |
| <i>n</i> -heptane | Activate carbon          | 75        | [8]          | Commercial                               |
| <i>n</i> -octane  | Ag-Y-zeolite             | 85        | [27]         | Commercial                               |
| <i>n</i> -octane  | Ni/Ce-Y zeolite          | 54        | [28]         | Liquid phase ion exchange                |
| <i>n</i> -octane  | Carbon nano-particles    | 72        | [29]         | Microwave oven                           |
| Cyclohexane       | Activated charcoal       | 99.4      | Present Work | Impregnation with Sn (II)                |



**Fig. 9.** SEM image of (a) raw/virgin AC after kerosene oil desulphurization, (b) Sn-AC after kerosene oil desulphurization, (c) raw/virgin AC after diesel oil desulphurization, (d) Sn-AC after diesel oil desulphurization.

aromatic sulfur species are present in diesel oil, which can act as bottleneck on the adsorbent surface [24]. It can be deduced from the current study that a large amount of aromatic sulfur species are adsorbed by the adsorbents from kerosene and diesel oil samples (Fig. 9)

A comparative study of the desulfurization efficiencies (i.e., % removal of DBT) of different adsorbents reported in literature for the desulfurization of the liquid fuels and the adsorbent used in the current study has been provided below in the Table 4. The data shows that the sulfur removal efficiency of the current adsorption system is still better than those of previously reported in the literature.

### 3.11. Regeneration study

For the industrial applications, the regeneration and subsequent recycling of the adsorbent are of vital importance. The regeneration experiments were performed after saturating the adsorbent with DBT at the optimized conditions and separating the adsorbent simply by filtration. The spent adsorbents were regenerated by washing with a number of solvents including methanol, acetonitrile, chloroform and toluene [22]. However, toluene showed best results in the regeneration of spent adsorbent for five successive regeneration cycles. Consequently, toluene was chosen as a suitable extractant for regeneration of the used adsorbents (Fig. 10).

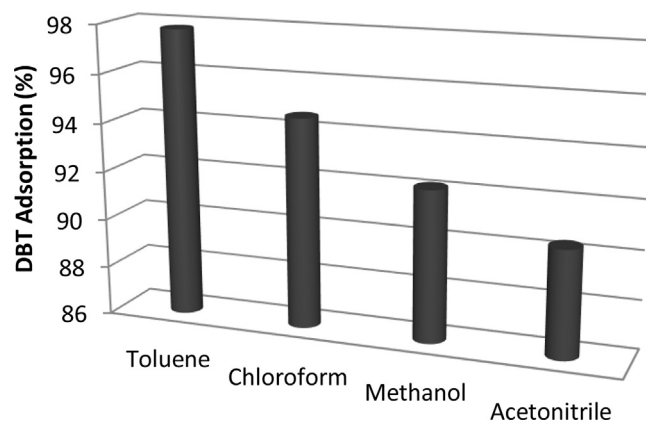
For every successful regeneration cycle of the spent adsorbent, about 5 mL of toluene per gram of adsorbent was used, the mixture was shaken at room temperature for 10 min. The regenerated adsorbent was filtered and dried in an oven below 100 °C for one hour, which was ready for reuse. It implies that the spent adsorbent is completely regenerable, and almost all adsorption capacity in the adsorbent can be recovered [30].

The economic feasibility of any industrial process can be judged from the cost of the consumables and its efficiency in comparison to other competitive processes. The sole industrial process for

desulfurization of petroleum is the HDS process, which is considered to be expensive processes because of requiring high temperature (400–600 °C), high H<sub>2</sub> partial pressure, expensive catalysts and a specialized reactor vessel for holding high temperature and high pressure. On the other hand the adsorption process under study operates under low temperature (below 100 °C), atmospheric pressure and require a simple reactor system. The consumables required include activated carbon with Sn impregnated from aqueous solution in very low concentrations. The adsorbent can further be regenerated by using low cost solvent toluene, and can be reused again upto 5 cycles without losing its efficiency.

#### 3.11.1. SEM analysis of regenerated Sn-AC adsorbent

It has been previously reported that the volume of micropores which governed the amount of DBT adsorbed, and the adsorption capacity is linearly related to the volume of these pores. It has



**Fig. 10.** DBT adsorption (%) as a function of modified Sn-AC, regenerated with various solvents.

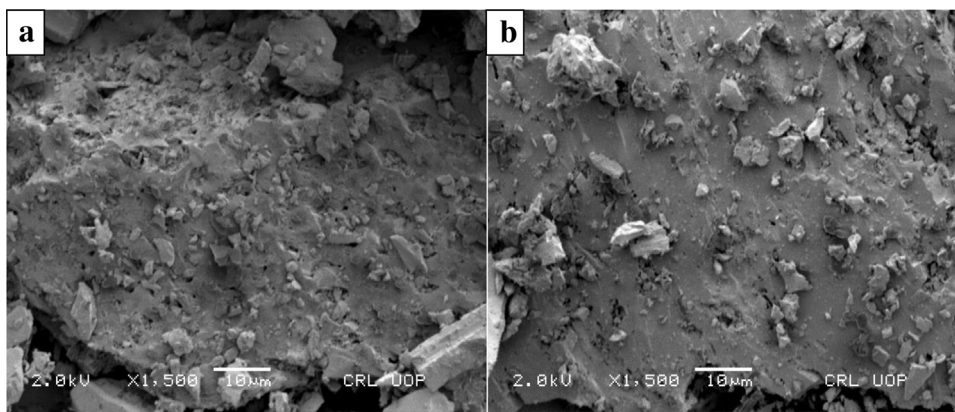


Fig. 11. SEM image of regenerated Sn-AC (a) before, (b) after five fold DBT adsorption.

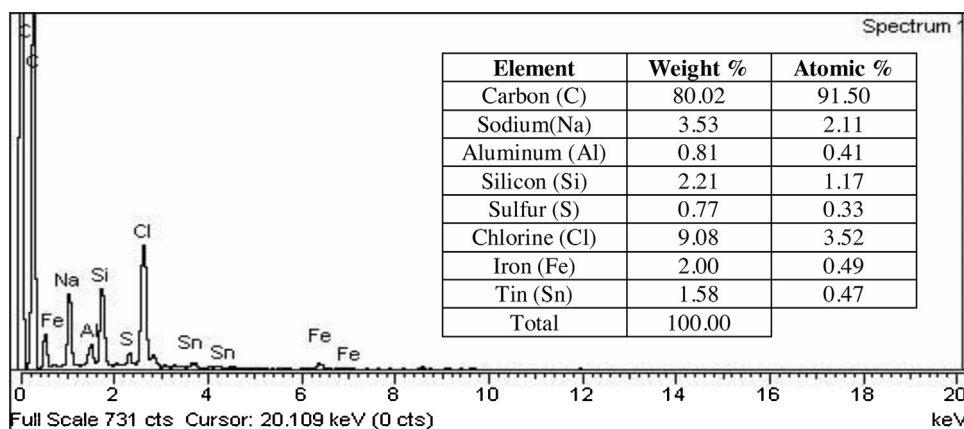


Fig. 12. EDX spectrum of regenerated Sn-AC after five folds DBT Adsorption.

also mentioned that mesopores controlled the kinetics of the DBT adsorption process [31].

When the adsorbent was regenerated by washing with toluene, the porosity was once again increased as shown in the Fig. 11(a), simply because DBT is more soluble in toluene and was washed away with the solvent. Fig. 11(b) shows micrograph of Sn-AC treated with DBT solution for five times. The porosity is almost absent due to the entrapment of DBT molecules in the pores.

### 3.11.2. EDX analysis of regenerated Sn-AC

Fig. 12 shows EDX profile of Sn-AC regenerated after five fold DBT adsorption. The increase in the percentage of carbon and sulfur suggests that DBT has been adsorbed. Moreover, Sn is present in less percentage which indicates that due to several time DBT adsorption and regeneration with toluene, a portion of Sn was leached away, however Sn is still present on the adsorbent surface, which play a pivotal role in the adsorption of DBT and can not be easily washed away completely with solvent washing. Hence the decrease in the percentage of Sn on the spent adsorbent surface can be overcome simply by loading  $\text{Sn}^{+2}$  through the wet impregnation technique. The elemental composition by weight percent and atomic percent of Sn-AC regenerated after five fold DBT adsorption is presented in the table.

## 4. Conclusions

The current study reveals that “Sn” impregnation on AC prominently increases its adsorption capacity in case of both model and real oil samples as compared to untreated AC. The DBT adsorption from the model oil was maximum under optimum conditions i.e.,

adsorbent dosage of 0.8 g, temperature of 60 °C and contact time of 1 h. The adsorption of DBT from model oil by Sn-AC follows pseudo second order kinetics. The adsorption data was found to best fit in the Langmuir adsorption isotherm as compared to Freundlich adsorption isotherm model. Compared to other available commercial adsorbents, modified AC is a cost effective, completely regenerable for multiple uses, highly efficient and selective for aromatic sulfur species. The current study will be helpful for the desulfurization of refractory aromatic compounds which cannot be removed from the commercial fuels effectively by other techniques and consequently, it will reduce the process cost and environmental problems associated with the presence of inherent sulfur.

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