Adsorption of Dibenzothiophene (DBT) on Activated Carbon from Dates’ Stones Using Phosphoric Acid (H₃PO₄)

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Abstract. Samples of Granular Activated Carbon (GAC) were produced from dates' stones by chemical activation using phosphoric acid (H₃PO₄) as an activator. Textural characteristics of GAC were determined by nitrogen adsorption at 77 K along with application of BET equation (Brunauer, Emmett and Teller) for determination of surface area. Pore size distribution and pore volumes were computed from N₂ adsorption data by applying the non localized density function theory (NLDFT). GAC samples were used in desulfurization of a model diesel fuel composed of n-decane (n-C₁₀H₂₂) and dibenzothiophene (DBT) as sulfur containing compound. The adsorption data were fitted to both Freundlich and Langmuir models with better predictions using Freundlich model. The optimum operating conditions for GAC preparation based on high adsorption capacity are T_carb = 600ºC, θ_carb = 3.0 hours and solid to activator weight ratio, R = 2.0 with adsorption capacity of 41.32 mg S/g of dry GAC. Finally, linear regression was done for the average pore diameter and the experimental data of micropore volume divided by the surface area using carbon slit pore model. The resulted linear empirical equation predicts reasonably the critical pore size diameter of DBT at which adsorption is hindered.

Keywords: Diesel fuel, Granular activated carbon, Phosphoric acid, desulfurization, Dibenzothiophene, Nitrogen adsorption.
1. Introduction

Due to the worldwide environmental pressures, fuel producers are facing challenges of producing extremely clean fuels. Special attention has been given to ultra-deep desulfurization of diesel fuel, to reduce the formation of acid rain and poisoning of catalysts in CO and NO\textsubscript{x} catalytic converters\textsuperscript{[1,2]}. Presently, the maximum allowable sulfur content in highway diesel fuel is reduced to less than 10 ppmw (part per million by weight) in the EU.

Although, methanol-based fuel cells\textsuperscript{[3,4]} are ideally operated with zero sulfur fuels\textsuperscript{[3,5]}, gasoline and diesel commercial fuels are still preferred, due to their high-energy content, availability, safety, and ease of storage. Therefore, acceptable sulfur concentration in fuel cells should be lowered to 0.1-0.2 ppmw.

Industrially, sulfur is reduced in fuels by catalytic hydrodesulfurization (HDS). However, this process has some hurdles such as the high operating temperatures (~ 300\textdegree C) and pressure (10-100 atm H\textsubscript{2}). Moreover, the process is hampered by the difficult removal of polyaromatic sulfur compounds such as dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT)\textsuperscript{[4]}. Extensive work has been done to reduce the sulfur content of diesel fuels from 500 to 15 ppmw including engineering of the HDS reactor and development of adsorbents to remove organic sulfur compounds either by complexation\textsuperscript{[6-12]}, generation of van der Waals, electrostatic interactions\textsuperscript{[13-15]} or by chemisorption at elevated temperatures\textsuperscript{[16,17]}. Among many others, McKinley and Angelici have shown preferential adsorption of DMDBT and DBT over decane on Ag\textsuperscript{+}/silica\textsuperscript{[18]}.

Effective adsorptive desulfurization is one of challenging research topics in clean fuel research because of the low-energy consumption, the ambient operation temperature and pressure and possibility of adsorbent regeneration\textsuperscript{[19-25]}.

Activated carbons (AC) are among the strong candidates for this purpose as inexpensive, easy to prepare in addition to the possibility of tailoring their structure, physical and chemical properties.\textsuperscript{[26]} They are also used for oxidative desulfurization\textsuperscript{[27]}.

Activated carbons can be prepared from agricultural and other wastes\textsuperscript{[28]}. Other forms of activated carbons are also employed for
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91 desulfurization of fuels include carbon aerogels [29], which have higher adsorption capacity due to the larger pore size [27]. Wang et al., prepared polystyrene-based activated carbon spheres with high adsorption capacity (153 mg/g), high surface area (up to 2022 m²/g) and large total pore volume (≥ 0.78 cm³/g) by KOH activation [4]. The adsorption capacity for this material revealed a good linear correlation with the volume of micropores rather than the surface area. The higher adsorption capacities of this material were correlated to the large quantity of acidic groups [4].

Very recently, desulfurization of model and commercial diesel fuel using GAC samples produced from dates’ stones by ZnCl₂ activation is reported [30,31]. Only 3 h were enough to adsorb 86% of DBT, nonetheless, after 48 h the adsorbed DBT reached 92.6% by GAC sample prepared with R = 0.5 at 700°C for 3h [30]. On the other hand, modeling of the Freundlich and Langmuir adsorption isotherms of 4,6-dimethyldibenzothiophene (4,6-DMDBT) as a single component and as a binary mixture with DBT on GAC activated by ZnCl₂ is explored in addition to other available binary adsorption models in the literature [31].

This paper investigates the removal of DBT from a model diesel fuel using granular activated carbon obtained by carbonization of dates' stones and activated by H₃PO₄. This material has shown very promising results in phenol and dye removal [32-34]. Effect of the preparation conditions on DBT removal will also be investigated.

2. Experimental

2.1 Preparation of GAC Samples

Dates' stones were obtained from local factories and washed several times with distilled water to remove the impurities and sticky contaminants. Dates' stones were then grinded to particle sizes ranging from 1.0 to 2.4 mm and sieved to different particle size fractions. Particles of an average sizes equal to 1.71 mm are chosen for preparation of GAC samples. H₃PO₄ was used for impregnation of these samples according to the procedure published elsewhere [28]. Preparation conditions of GAC samples cover the carbonization temperature, T_carb (500, 600 and 700°C), R, [0.5 and 2.0] and carbonization time, θ_carb (1 and 3 h).
2.2 Nitrogen Adsorption Measurements

Specific surface area, pore size distribution (PSD), micro, meso and macroporosity of the produced GAC were determined. Physical adsorption of $N_2$ at 77 K using an automatic adsorption system (NOVA2200e, Quantachrome). The equipment was connected to a rotary van vacuum pump (Pfeiffer vacuum) which can achieve a final pressure $< 6 \times 10^{-5}$ mbar and exhaust pressure 250-1500 mbar. True densities of GAC samples are first determined using a micropycnometer (qunatachrome). GAC sample is thereafter degassed at 573 K under vacuum and then cooled to room temperature. Nitrogen gas (AHG, 99.99%) is used as the adsorbate. All the adsorption isotherms are 42 points isotherms; 23 adsorption point + 19 desorption points in the range of $P/P^0$ = 0.005 to 0.99.

NOVAWin2 (Quantachrome Instrument) data analysis software \[35\] was used to calculate other parameters such as multipoint BET \[36\], single point BET, Langmuir surface area determinations, thickness, pore size were also measured. The adsorption/desorption isotherms are used to find out BET surface area, pore volume and pore size distribution. Various characteristics of the GAC such as pore size distribution (PSD), average pore size ($d_p$), $(V_t)_{NLDFT}$, are obtained from adsorption isotherm data using the software, where; $(V_t)_{NLDFT}$ is total pore volume estimated using NLDFT \[37\], $V_{mic}$ is micropore volume (pore sizes less than 2 nm) determined from NLDFT and $V_{meso}$ is pore volume for pore sizes between 2 and 50 nm and it is taken as the difference between $(V_t)_{NLDFT}$ and $V_{mic}$.

2.3 DBT Adsorption Measurements

The concentration of DBT in the model diesel fuel is determined using a Shimadzu GC 17AATFW-V3 gas chromatograph equipped with Rxi-5ms capillary column, 30 m × 0.53 mm ID (Restek) and FID detector. Excellent separation of DBT and 4,6-DMDBT is obtained when the injection port temperature is 260ºC, the column oven temperature is adjusted to 150ºC for 3.4 min followed by heating up to 200ºC at rate of 20ºC/min. Detector temperature was set to 250ºC and column pressure at 50 kPa.

Amount of 10 ml (7.2436 g) of model diesel fuel as n-decane (n-$C_{10}H_{22}$) containing 500 part per million by weight of sulfur (ppmwS) as
DBT was placed in 50 ml Stoppard glass bottles. A known weight of GAC was added to each bottle and then placed in an orbital shaker at room temperature. Shaking was performed to ensure a reasonably good relative movement between GAC particles and the liquid. It has been previously reported that, an equilibration time is 48 h is optimum for attainment of equilibrium \[30\]. After which, a sample is withdrawn, filtered on filter paper and the filtrate is subjected to GC analysis using tetradecane as internal standard (IS).

### 3. Results and Discussions

#### 3.1 Nitrogen Adsorption Measurements

Figure 1 shows a comparison between the pore size distribution (determined from NLDFT using NOVAWin2 software for quantachrome) for two GAC samples produced at carbonization temperature of 700°C and carbonization time of 3 h using two different ratios of H\textsubscript{3}PO\textsubscript{4} to dates' stones (R). When R = 0.5, essentially a microporous GAC with a narrow PSD mainly in micropore region and centered around 1.4 nm is obtained. The pore volume in this case is only 0.2019 cm\textsuperscript{3}/g. On the other hand, increasing R to 2 produces GAC with a bimodal particle size distribution (PSD) in the microporore and mesopore region. In the micropore region a broad PSD is obtained with maximum at 1.36 nm whereas in the mesopore region there is a maximum at about 4.9 nm. However, the pore volume in this case (R = 2) is more than tripled to 0.6963 cm\textsuperscript{3}/g compared to 0.2019 cm\textsuperscript{3}/g when R was equal to 0.5. Also, increasing R from 0.5 to 2 increases BET surface area from 348.7 to 771.5 m\textsuperscript{2}/g.

Table 1 summarizes the main textural characteristics of the produced GAC using H\textsubscript{3}PO\textsubscript{4} as activator. The BET surface area and pore volume decrease with increasing the carbonization temperature for both carbonization times and R=0.5 due to the sintering effect at high temperature, the subsequent shrinkage of the GAC, and finally, realignment of the structure which resulted in reduced pore areas as well as volume \[38\]. However, GAC samples with larger BET surface area and larger pore volume are obtained at R=2.
Fig. 1. Comparison between pore size distribution (PSD) for two GAC samples produced at carbonization temperature of 700ºC and carbonization time of 3 hours using two different ratios of H₃PO₄ to dates’ stones (R).

Table 1. Structural characteristics of GAC from dates’ stones produced by H₃PO₄ activation.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>T_{carb} (ºC)</th>
<th>θ_{carb} (h)</th>
<th>R</th>
<th>BET area (m²/g)</th>
<th>( V_t ) (cm³/g) (p/p⁰ = 0.98)</th>
<th>Parameters estimated by NLDFT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(( V_t )_NLDFT cm³/g)</td>
</tr>
<tr>
<td>DDS-1</td>
<td>500</td>
<td>1</td>
<td>0.5</td>
<td>705</td>
<td>0.3611</td>
<td>0.315</td>
</tr>
<tr>
<td>DDS-2</td>
<td>500</td>
<td>1</td>
<td>2.0</td>
<td>418.9</td>
<td>0.3956</td>
<td>0.366</td>
</tr>
<tr>
<td>DDS-3</td>
<td>500</td>
<td>3</td>
<td>0.5</td>
<td>631.2</td>
<td>0.3295</td>
<td>0.312</td>
</tr>
<tr>
<td>DDS-4</td>
<td>500</td>
<td>3</td>
<td>2.0</td>
<td>343.2</td>
<td>0.3343</td>
<td>0.314</td>
</tr>
<tr>
<td>DDS-5</td>
<td>600</td>
<td>1</td>
<td>0.5</td>
<td>770</td>
<td>0.3915</td>
<td>0.373</td>
</tr>
<tr>
<td>DDS-6</td>
<td>600</td>
<td>1</td>
<td>2.0</td>
<td>560.1</td>
<td>0.6026</td>
<td>0.555</td>
</tr>
<tr>
<td>DDS-7</td>
<td>600</td>
<td>3</td>
<td>0.5</td>
<td>562.8</td>
<td>0.2872</td>
<td>0.275</td>
</tr>
<tr>
<td>DDS-8</td>
<td>600</td>
<td>3</td>
<td>2.0</td>
<td>442.4</td>
<td>0.437</td>
<td>0.41</td>
</tr>
<tr>
<td>DDS-9</td>
<td>700</td>
<td>1</td>
<td>0.5</td>
<td>282</td>
<td>0.1815</td>
<td>0.167</td>
</tr>
<tr>
<td>DDS-10</td>
<td>700</td>
<td>1</td>
<td>2.0</td>
<td>674.9</td>
<td>0.6354</td>
<td>0.597</td>
</tr>
<tr>
<td>DDS-11</td>
<td>700</td>
<td>3</td>
<td>0.5</td>
<td>347.8</td>
<td>0.2019</td>
<td>0.189</td>
</tr>
<tr>
<td>DDS-12</td>
<td>700</td>
<td>3</td>
<td>2.0</td>
<td>771.5</td>
<td>0.6963</td>
<td>0.656</td>
</tr>
</tbody>
</table>

\( T_{carb} \) = carbonization temperature, ºC; \( \theta_{carb} \) = carbonization time, h; \( R \) = impregnation ratio; \( V_t \) = total pore volume, cm³/g; (\( V_t \)\_NLDFT cm³/g) = total pore volume estimated by NLDFT, cm³/g; \( V_{meso} \) = mesopore volume estimated by NLDFT, cm³/g; \( V_{mic} \) = micropore volume estimated by NLDFT, cm³/g; \( d_p \) = average pore size, nm.
The pore volume strongly depends on the impregnation ratio (R) as it almost doubled when the ratio is increased from 0.5 to 2.0 for all carbonization temperatures. But, increasing R at 500°C and 600°C carbonization temperature decrease BET surface area while it increases at 700°C.

When the carbonization time is increased from 1 to 3 h the same trend is observed for the BET area while the pore volume decreases at 500°C and 600°C carbonization temperature and increase at 700°C. Generally average pore size increases with increasing R and it decreases at 700°C. Based on these trends carbonization temperature at 700°C yield high BET, high pore volume but low pore size which might not be appropriate for high adsorption capacity.

The total pore volume at \( \frac{P}{P^0} = 0.98 \) significantly increases by increasing R from 0.5 to 2.0 which inlines with reported results\cite{39} and could be correlated to \( H_3PO_4 \) on the outer parts of carbon particles which widens the porosity by localized decomposition of the organic matter. This process results in enhancement of the meso- and macropore formation.

Values of the total pore volume were estimated by the non localized density function theory (NLDFT) assuming cylindrical pore model which appears slightly lower than those predicted from the nitrogen adsorption data. These differences can be due to imperfect cylindrical pores of the GAC samples.

### 3.2 DBT Removal by GAC Produced Using \( H_3PO_4 \)

Adsorption isotherms of DBT from model diesel fuel are fitted to both Freundlich and Langmuir isotherms, equations (1) and (2), respectively.

\[
Xe = k(Ce)^{1/n}
\]  

Where \( Xe \) is the amount of sulfur adsorbed (mg S/g of dry GAC), \( Ce \) is the equilibrium concentration of S in solution (ppmwS), \( k \) and \( n \) is the Freundlich constants

\[
q_e = q_m \frac{K_L Ce}{1 + K_L Ce}
\]
Where $K_L$ is the Langmuir adsorption constant which indicates the relative affinity of the adsorbate toward the surface of the adsorbent, $q_m$ is the maximum adsorption capacity (mg S/g of dry GAC).

Figures 2(a, b and c) show the Freundlich isotherm for adsorption of DBT on GAC prepared using H$_3$PO$_4$ for two carbonization times ($\theta_{\text{carb}}$) and two ratios (R), for carbonization temperatures ($T_{\text{carb}}$) of 500, 600 and 700ºC respectively. For all adsorption measurements the average particle size was 0.75 mm and the adsorption temperature was 23±1ºC. The adsorption data were fitted to both Freundlich and Langmuir isotherms and the parameters of these isotherms were determined using non linear regression. Figure 2(a) shows that at $T_{\text{carb}}=500ºC$, the effect of changing $\theta_{\text{carb}}$ and R is not significant. However, at higher equilibrium concentration, GAC adsorbs more when R is increased from 0.5 to 2.0. Figure 2(b) shows that at $T_{\text{carb}}=600ºC$ the adsorption amount is higher compared to $T_{\text{carb}}=500ºC$. Figure 2(c) shows that the amount adsorbed is increased when $\theta_{\text{carb}}$ is increased from 1h to 3 h at R = 0.5 due to the increase of the corresponding BET surface areas from 282 m$^2$/g ($V_t$=0.1815 cm$^3$/g, $d_p$=1.022 nm) to 347.8 m$^2$/g ($V_t$=0.2019 cm$^3$/g, $d_p$=1.328 nm) while the effect of $\theta_{\text{carb}}$ change is negligible at R = 2.0 as indicated corresponding change is (BET=674.9 cm$^3$/g, $V_t$=0.635 cm$^3$/g, $d_p$=1.169 nm) at $\theta_{\text{carb}}$ =1h to (BET=771.5 cm$^3$/g, $V_t$=0.6963 cm$^3$/g, $d_p$=1.169 nm) at $\theta_{\text{carb}}$=3h. On the other hand, increasing R from 0.5 to 2 significantly increases the amount adsorbed for both $\theta_{\text{carb}}$ of 1 and 3 h. This is evidenced from the GAC properties which show that increasing R from 0.5 to 2 corresponds to BET surface area increase from 282 m$^2$/g to 674.9 m$^2$/g at $\theta_{\text{carb}}$ = 1h and from 347.8 m$^2$/g to 771.5 m$^2$/g at $\theta_{\text{carb}}$ =3 h. It can be shown from Fig. 2(c) that the lowest adsorption amount at $T_{\text{carb}}=700ºC$ is observed by the lowest values of BET area (282 m$^2$/g), pore volume (0.1815 cm$^3$/g) and pore size (1.022nm) exhibited by GAC at $\theta_{\text{carb}}$ =1h and R=0.5. As shown in Table 2, $R^2$ range from 0.962 to 0.999 when fitting adsorption data using Freundlich isotherm, while for Langmuir isotherm $R^2$ range from 0.913 to 0.990. Freundlich isotherm represents the adsorption data of DBT on GAC better than Langmuir isotherm in the range of the concentration studied. This is consistent with fact that Langmiur isotherm is derived with the assumption that the surface of the adsorbent is homogeneous. This is not usually the case with GAC which has highly heterogeneous surfaces. Nevertheless, the Langmuir isotherm
was also used to estimate the maximum adsorption capacity, $q_m$, which is used widely to compare the quality of different adsorbents.

Figures 3 and 4 show $k$ and $q_m$ values respectively for all GAC samples prepared at various carbonization temperatures, carbonization times and ratios using $\text{H}_3\text{PO}_4$.

![Fig. 2. Freundlich isotherms for adsorption of DBT on GAC samples prepared using $\text{H}_3\text{PO}_4$ at different carbonization time and ratios. Carbonization temperatures = 500°C,(a); 600°C, (b) and 700°C, (c). Particle size =0.75 mm. Adsorption temperature = 23±1°C.](image)

Table 2. Freundlich and Langmuir isotherms constants and their corresponding correlation coefficients and 95% confidence intervals for DBT adsorption by GAC produced from dates stones at different conditions using $\text{H}_3\text{PO}_4$ as activator.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Freundlich isotherm parameters</th>
<th>Langmuir Isotherm parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n$ (95%)</td>
<td>$k$ (mg/g) (95%)</td>
</tr>
<tr>
<td>DDS-1</td>
<td>1.460</td>
<td>0.451</td>
</tr>
<tr>
<td>DDS-2</td>
<td>1.295</td>
<td>0.419</td>
</tr>
<tr>
<td>DDS-3</td>
<td>2.143</td>
<td>0.169</td>
</tr>
<tr>
<td>DDS-4</td>
<td>1.184</td>
<td>0.365</td>
</tr>
<tr>
<td>DDS-5</td>
<td>2.349</td>
<td>0.667</td>
</tr>
<tr>
<td>DDS-6</td>
<td>2.014</td>
<td>0.141</td>
</tr>
<tr>
<td>DDS-7</td>
<td>1.523</td>
<td>0.724</td>
</tr>
<tr>
<td>DDS-8</td>
<td>1.600</td>
<td>0.675</td>
</tr>
<tr>
<td>DDS-9</td>
<td>2.002</td>
<td>0.985</td>
</tr>
<tr>
<td>DDS-10</td>
<td>2.178</td>
<td>1.165</td>
</tr>
<tr>
<td>DDS-11</td>
<td>2.997</td>
<td>0.808</td>
</tr>
</tbody>
</table>
Fig. 3. $k$ for adsorption of DBT by GAC produced at various carbonization temperatures, carbonization times and ratios using $H_3PO_4$ as an activator.

GAC sample prepared at ($T_{\text{carb}} = 500^\circ\text{C}$, $\theta_{\text{carb}} = 1\text{h}$ and $R = 0.5$) the experimental data fails to fit Freundlich as well as Langmuir isotherms. The highest $k$ value of 2.731 is obtained at ($T_{\text{carb}} = 700^\circ\text{C}$, $\theta_{\text{carb}} = 3\text{h}$ and $R = 2.0$) and the maximum value obtained for $q_m$ is 41.32 at ($T_{\text{carb}} = 600^\circ\text{C}$, $\theta_{\text{carb}} = 3\text{h}$ and $R = 2.0$). As a compromise the selected optimum conditions to produce GAC using $H_3PO_4$ that yield high values of $k$ and $q_m$ are at carbonization temperature ($T_{\text{carb}}$) = 600 °C, carbonization time ($\theta_{\text{carb}}$) = 3 hours and ratio of $H_3PO_4$ to dry dates’ stones ($R$) = 2.0.

Fig. 4. $q_m$ for adsorption of DBT by GAC produced at various carbonization temperatures, carbonization times and ratios using $H_3PO_4$ as an activator.
3.3 Comparison with GAC Activated by ZnCl₂

Comparing the adsorption data of GAC samples activated by H₃PO₄ with samples activated by ZnCl₂ under the same preparation conditions reported previously [30], relatively lower adsorption amounts are observed by samples prepared by phosphoric acid activation. The reported adsorption capacity, qₘ, for ZnCl₂-activated GAC samples ranged from 21.89 to 42.56 mg S/g dry GAC whereas in case of H₃PO₄-activated samples is in the range of 17.27 to 41.32 mg S/g dry GAC. On the other hand lower k values and higher n (low 1/n) values confirm the lower adsorption capability of H₃PO₄ compared to that produced using ZnCl₂. The higher adsorption capacity of ZnCl₂ samples maybe attributed to the higher BET area (802.0-1270.0 m²/g), pore volume (0.442-1.647 cm³/g) and pore diameter (1.289-1.884 nm) compared to the corresponding ones for H₃PO₄ (282.0-771.5 m²/g), (0.182-0.696 cm³/g) and (1.022-1.447 nm).

3.4 Comparison with Different Adsorbents

Several recent studies were conducted for removal of DBT from model diesel using different adsorbents prepared at various conditions. Every adsorbent is characterized by its own adsorption capacity depending on the preparation procedure including the activator used and if a heat treatment is also applied. Table 3 shows the comparison of each adsorbent based on qₘ value. However, GAC samples prepared in this work achieved higher adsorption capacity of 41.32 mg S/g dry GAC than most of the recently reported adsorption capacities.

### Table 3. Comparison of different adsorbents based on qₘ.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity, mg S/g</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon aerogel</td>
<td>15.06</td>
<td>[40]</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>41.53</td>
<td>[41]</td>
</tr>
<tr>
<td>GAC from dates' stones</td>
<td>35.0</td>
<td>[30]</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>21.02</td>
<td>[42]</td>
</tr>
<tr>
<td>GAC from dates' stones</td>
<td>41.32</td>
<td>Present work</td>
</tr>
</tbody>
</table>

3.5 DBT Critical Diameter Prediction

If we define the area based adsorption capacity term, Q, as

\[
Q = \frac{q_m}{\text{surface area}}
\] (3)
The surface area of the micropore volume (pore sizes less than 2 nm) was determined from the surface area - pore size distribution which was obtained by fitting the adsorption data using the carbon slit pore model.

Figure 5 shows the effect of average pore diameter determined by NLDFT on the calculated Q values using equation (3). Linear regression was used to fit the data with $R^2$ of 0.54. The resulted linear regression equation is

$$Q = 4.474d_p - 4.296$$

(4)

When solving equation (4) for the diameter below which no adsorption takes place (critical diameter), the following value is obtained

$$d_p = \frac{4.296}{4.474} = 0.960 \text{ nm}$$

Although this value is greater than the reported critical diameter of DBT as 0.8 nm, it reasonably satisfies what previous studies suggested that DBT adsorption is hindered by the GAC with critical pore diameter close to 0.8 nm $^{[43]}$ and the adsorption of DBT on the GAC sample is mainly physical. However, when the same analysis was made to the GAC samples activated by ZnCl$_2$, the $d_p$ value obtained from the linear correlation was 0.80 which matches the critical diameter of DBT $^{[30]}$.

![Fig. 5. Effect of average pore diameter on $q_m$.](image)
4. Conclusions

Selective adsorption of DBT using activated carbon activated prepared by $\text{H}_3\text{PO}_4$ activator and prepared at different conditions from dates' stone is feasible, promising and worth further studying. The obtained adsorption data can be represented by both Freundlich and Langmuir isotherms. However, Freundlich isotherm fits the data more accurately. Higher $T_{\text{carb}}$ and $\theta_{\text{carb}}$ and R ratio are preferred for higher adsorption capacity of the GAC samples. Activated carbon with higher BET surface area, higher pore volume and higher average pore size has a higher adsorption capacity. Also, GAC samples activated by $\text{ZnCl}_2$ showed higher adsorption capacity due to higher BET surface area, higher pore volume and higher average pore size. Regression analysis was done for the average pore diameter and the experimental data of micropore volume divided by the surface area. The resulted linear empirical equation predicts reasonably the critical pore size diameter that is close to the molecular size of DBT at which adsorption is hindered.

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References


ادمتصاص مادة الدايبينزوثيريفين على الكربون النشط الحبيبي المنتج من نوى التمر باستخدام حمض الفوسفوريك

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المستخلص. تم تحضير عينات من الكربون النشط الحبيبي المنتج من نوى التمر باستخدام حمض الفوسفوريك، كما تم تحديد الخواص السطحية للكربون باستخدام ادمتصاص النتروجين عند درجة حرارة 77 كلفن، ونظرية التغيير غير الموضح للكثافة لإيجاد أبعاد المسامات وأحجامها (NLDFT)، ومعادلة LEBET لقياس المساحة السطحية.

ولقد استخدمت عينات الكربون بعد ذلك لإزالة مركب الكبريت من وقود ديزل نموذجي مكون من مادة الديكان (n-C_{19}H_{22}) مضافاً إلى مادة الدايبينزوثيريفين (DBT) كمركب للكبريت.

وقعت نتائج ادمتصاص المخبرية على نموذج الرياضيين، و (Freudlich) (Langmuir) وب (Freudlich) يعطي نتائج أفضل، مما وجد أيضاً أن أفضل الظروف التحضيرية لإنتاج الكربون النشط الحبيبي المنتج من نوى التمر، باستخدام حمض الفوسفوريك، بناء على أعلى سعة للادمتصاص عندما تكون درجة حرارة الكربون = 600 درجة مئوية.
Adsorption of Dibenzothiophene (DBT) on Activated...

For a period of 3 hours, and a ratio of phosphorus to weight of the sample of 2.

When analyzing the results, the results of the rational, by the assumption of the dimensions of the materials of dibenzothiophene.

يمكن أن تتنبأ بقياس أبعاد المسامات لمادة الدابينزوثيوفين.