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Synthesis and Characterization of Acidic Activated Carbon from Corncobs for Adsorption Desulfurization of Simulated Crude Oil

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ABSTRACT

Corncob is an agricultural biomass waste that was widely investigated as an adsorbent of contaminants after transforming it into activated carbon. In this research carbonization and chemical activation processes were achieved to synthesize corncob-activated carbon (CAC). Many pretreatment steps including crushing, grinding, and drying to obtain corncob powder were performed before the carbonization step. The carbonization of corncob powder has occurred in the absence of air at a temperature of 500 °C. The chemical activation was accomplished by using HCl as an acidic activation agent. Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) facilitated the characterization of CAC. The results showed the CAC has non-uniform morphological features with different shapes of its active sites. The prepared CAC was utilized in adsorption of sulfur in its highly complex form of dibenzothiophene (DBT). Particular adsorption parameters of contacting time, temperature, and adsorbent dose were optimized to select the best conditions. These certain conditions are then applied in the adsorption of different DBT concentrations. The maximum removal of DBT reached around 83% at optimal conditions of contacting time (30 min), temperature (60 °C), and adsorbent dose (3 gL^{-1}) . The removal efficiency was significantly increased by decreasing the initial concentration of DBT. The experimental data fitted well with the Freundlich isotherm model compared with the Langmuir one. The maximum capacity of CAC for adsorption of DBT at equilibrium was 833.3 mg·g⁻¹ at 60 °C. The findings of this research introduce the CAC as a feasible adsorbent for removal DBT from simulated liquid petroleum fuels.

Keywords: corncob; biomaterial-adsorbent; acid activation; activated carbon; dibenzothiphene**.**

INTRODUCTION

Crude oil a mixture of hydrocarbons contains a variety of sulfur compounds. These compounds are different in their constituents and vary from the very simple free sulfur element (S) to very complex dibenzothiophene $(C_{12}H_8S)$. These species are ultimately distributed in different oil cuts via refining processes. The sulfur content in crude oils ranges between about 0.1–5% wt. for sweet and sour crudes respectively [1]. In the majority of crude oils, dibenzothiophenes (DPT) and some other thiophenes account for approximately 70% of the total sulfur content [2, 3]. Through processing, refining, and firing, sulfur compounds transform into other forms, mainly as released SO_2 and H_2S gases, which are harmful to the echo system. Conversion

processes are essential to reduce sulfur contents in each oil product via conventional hydrodesulfurization (HDS) and sulfur recovery unit (SRU). These approaches are classified as extremely costly and energy-intensive technologies. On the other hand, utilizing HDS on bulk crude oil is ineffective at removing certain refractory sulfur compounds. Therefore, alternative desulfurization techniques of crude oil and/or its products are indispensable [4].

Adsorption is a promising energy-effective alternative desulfurization technology, particularly when utilizes natural and even waste materials [5]. Activated carbon derived from agricultural wastes like corncobs can provide a viable sustainable adsorbent option [6]. Industrialization of adsorption strategies in sulfur remedies, consuming corn wastes as activated carbon, not only serves in energy conservation but also in valorization of' agricultural residues [7, 8]. Due to its porous structure and high surface area, corncob is a favorable feedstock substance for producing activated carbon. Numerous industries have employed activated carbon derived from corncobs [9, 10]. Significantly, corncobs present as an attractive renewable feedstock for synthesizing activated carbons in desulfurization applications [11]. Synthesizing of activated carbons from corncobs for these purposes occurs via the carbonization of raw material at about 500–900 °C followed by physical or chemical treatments, targeting the increase of porosity and surface area [11, 12]. In the physical activation scenario, the carbonized material is subjected to an oxidizing atmosphere (typically oxygen, steam, or carbon monoxide) at a temperature window of around 600–1200 °C [13]. Chemical activation, on the other hand, involves the use of chemical agents including strong/weak acids, strong bases, or salts. In practice, the chemical pathway is the more favorable as it requires lower temperature and shorter activation time [13, 14].

The desulfurization of sulfur compounds from hydrocarbon streams depends on the adsorption technique in which these constituents are captured and removed [15]. Due to its high surface area, porous structure, and surface chemistry, activated carbon derived from corncobs is one of the most desired adsorbents [16–18]. Deep insight into the adsorption of sulfur compounds (hardly the DBT) using corncobs activated carbon to enhance cleaner and more sustainable energy production is rarely in the literature. The current work focuses on a novel ultraclean desulfurization process of model oil by the adsorption strategy using acid-treated activated carbon derived from corn wastes, particularly corncobs as an adsorbent. Effective parameters including contact time, adsorbent dose, initial concentration of DBT, and temperature were investigated with the use of Models of adsorption, particularly Langmuir and Freundlich isotherms, to assist in forecasting adsorption behavior and examine the experimental data.

METHODOLOGY

Material

The current study has employed corncobs as raw material which has been delivered from a local central vegetable store in Diyala province, central-eastern part of Iraq. The simulated oil feedstock was an analar grade n-hexane (> 99% purity) which was commercially obtained from CDH Chemicals Lts. The applied activation agent was a concentrated grade of hydrochloric acid HCl (35%), which was diluted to obtain (HCl 2.0M). The sulfur constituent was dibenzothiophene (DBT). Both HCl and DBT were supplied by Sigma-Aldrich Company.

Methods

The experimental work mainly involved three stages; (1) obtaining and carbonizing corncob powder, (2) activating the corncob-based carbon, and (3) removing/desulfurizing DPT from the simulated crude oil (n-hexane).

Preparation of carbonized corncob powder

The corncob waste material was first converted to powder, and then it was carbonized to produce the corncob carbon. The waste corncob was obtained from fresh corn after removing the seeds (kernels). The cobs were thoroughly cleaned and dried under direct exposure to sunlight for three days in an environmental temperature range of between $(35-40 \degree C)$. After that, the corncobs were catted into small pieces with volumes of around 1–3 cm3 . Further drying was performed in an electric oven at 80 °C for 6 h with a constant stirring time of 1 min for every 1 h of heating. Then, the segments of the corncobs were crushed, ground, and sieved to less than 600 µm to be ready for the carbonization and altimetry of the activation processes [14]. Carbonization of corncob powder was carried out by using a suitable amount of ground corncob powder of about 200 g. This quantity was placed in pre-weighed crucibles, and inserted in a muffle furnace at 500 ºC for 10 min in the absence of oxygen. The crucible was then left to cool down inside the furnace for 24 hours. After that, the carbonized corncob was then stored in an airtight container for further treatment.

Preparation and characterization of corncob-activated carbon

The activation process of corncob-based carbon was accomplished via acid treatment, where 100 g of the carbonized corncob was leached with 75 ml of hydrochloric acid (2.0 M) in a 150 ml glass beaker for 24 hours [14]. Then, the mixture was filtered through a filter paper. After that, the residue was washed with fresh water until the pH of the washing water attained 7. The residue was then dried at room temperature (about 32 °C) for around 24 hours to be ready for further experimental work of desulfurization tests.

Characterization of the produced corncobactivated carbon (CAC), i.e. surface area, surface morphology, crystallography, and microstructure is accomplished using scanning electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy respectively. The pH meter was used to measure the acidity of the wash water of residual ACA that was treated with HCl.

Desulfurization experiments

Experiments of desulfurization tests were conducted in a batch process, developing an ultraclean process for desulfurization of the most complex sulfur compounds (DBT) from model crude oil (n-hexane) via an adsorption technique using the acid-treated CAC as an adsorbent material. The procedure involved using a graham condenser, double neck round flask (250 mL), mantle magnetic stirrer heater, thermometer, and beaker (1 L). The setting of runs is as presented in Figure 1. The same setting was applied in the dissolving of solid DBT material.

Simulated oil was prepared an adequate amount (3 L) by dissolving DBT in the n-hexane [19]. The concentration of the DBT was 400 ppm. The process occurred at 60 °C for around 25 min. The sulfurized hexane (SH) was then cooled down and kept in a well-closed container. For each desulfurization run,

50 mL of (SH) feedstock was used to be treated with CRC adsorbent. The studied parameters were the dose of CAC, amounts of DBT, contacting time, and temperature in rages of $1-5$ gL⁻¹, $100-$ 400 ppm, 5–35 min, and 30–50 °C respectively. Sets of runs were carried out in which only one parameter was changed in each set, while others remained constant. The solution was then filtered by using a filter paper, after that the filtrate was prepared for sulfur content measurement. The sulfur content apparatus facilitated the measurement of the remaining sulfur in the simulated crude oil (n-hexane). These measurements were carried out in the Iraqi Petroleum Research and Development Center (PRDC), bub-alsham-Baghdad. However. The estimated error for the DBT removal (calculated for three reiterated tests) is around 2% for all experiments.

Adsorption isotherms

Langmuir and Freundlich's isotherms are the most common models that can illustrate the distribution of molecules between the liquid and solid phases at equilibrium [20, 21]. These models can also significantly describe surface phenomena. Employing such models provides considerable knowledge regarding the designing and optimizing desulfurization processes [22]. The adsorption of sulfur in an aqueous solution by using CAC has been investigated in the current work via the two isotherm models of Langmuir and Freundlich as

Figure 1. Experimental setting of a simulated crude oil (n-hexane) desulfurization process via adsorption method using activated carbon derived from corncobs as an adsorbent material

depicted in Equations 1 and 2 to fit the experimental data and determine the corresponding characteristic constants. The Langmuir isotherm model [23] portrays the monolayer adsorption scenario on uniform adsorption sites which can be displayed as follows [24, 25]:

$$
\text{Langmuir model} \quad \frac{\mathcal{C}_e}{q_e} = \frac{\mathcal{C}_e}{q_m} + \frac{1}{K_L q_m} \qquad (1)
$$

- pletely covered with DBT $(mg·g⁻¹), C_e$ is 1 capacity when the CAC surface is comwhere: q_m is the theoretical maximum adsorption the equilibrium concentration of DBT in the solution (mg·L⁻¹), q_e is the amount of DBT adsorbed at the specified equilibrium $(\text{mg} \cdot \text{g}^{-1}), K_L^{\dagger}(\text{L} \cdot \text{mg}^{-1})$ is a constant that is related with the adsorption energy. Freundlich equation, on the other hand, is an empirical equation that was suggested by Freundlich [26] to define the sorption performance of solutes on heterogeneous surfaces. This model can be mathematically expressed by the following equation [25, 27]: $\frac{1}{11}$
- Freundlich model $\ln q_e = \ln K_F + \frac{1}{n}$ $\frac{1}{n}$ ln C_e ⁽²⁾ the broad where: K_F (mg·g⁻¹) and $1/n$ (L·mg⁻¹) are the
- Freundlich constants that represent the adsorption capacity and intensity.

RESULTS AND DISCUSSIONS

Characterization of CAC

Surface area and pore volume

The produced CAC had a Brunauer-Emmett-Teller surface area of $177.66 \text{ m}^2\text{g}^{-1}$ with a pore volume of 0.07 cm^3 g⁻¹. In comparison to another study that employed the acidic activation route, the BET and pore volumes were 1069 m^2g^{-1} and 1 cm^3g^{-1} respectively [14]. These values are higher than what obtained in the current study which could be because they used a high concentration of H_3PO_4 (50%) before a long carbonization time of 120 min at 500 °C and an additional course of grinding after the carbonization and activation process. Using highly concentrated H_2SO_4 (95–98%) without heating and additional grinding produced a low BET surface area of only $1.65 \text{ m}^2\text{g}^{-1}$ and a total pore volume of 0.005 cm³g⁻¹ [28]. It has been reported that the concentrated acid containing sulfate, nitrate, and phosphate could be responsible for the augmentation of

bon before acidic activation are 136.89 m^2g^{-1} which C_a is From the comparison of the data obtained with the oxygen on the surface of different activated carbons and the limitation of the total pore volume and activity of adsorption [29]. Furthermore, neutralization of the pH value of the highly concentrated acids should require high water amounts, and heating samples at 500 °C for 120 min could be an energy consumption technique. The BET measurements for corncob caris lower than of CAC by only about 23%. The total pore volume of the corncob carbon, on the other hand, is $0.09 \text{ cm}^3 \text{g}^{-1}$ which is higher by about 29%. literature, one can suggest that the carbonization of corncob carbon after acid treatment is more efficient in terms of surface area and total pore volume. Also, for no further grinding, HCl presents as a better choice for enlargement surface area and no more production of surface-oxygen contents.

XRD analysis

The CAC produced from corncob via carbonization and acidic activation processes can be crystallographically characterized by the aid of X-ray diffraction as presented in Figure 2. From Figure 2, the broadening of the background diffraction of the activated carbons derived from corncob denotes that the (AC) predominantly has an amorphous structure [30]. The XRD measurement displays two broad peaks that are centered at 2-theta values of around 24.5° and 43.5° respectively. These broad peaks are appointed to the reflection from $(0 0 2)$ and $(1 0 0)$ planes which are related to residuals of crystalline carbon of expanded lattice parameters. In addition, the existence of two small sharp peaks is observed in 2-theta magnitudes of 28° and 40°. The presence of these peaks could be assigned to the existence of minor amounts of undefined impurities. Bragg and Scherer equation was applied to calculate the interlayer spacing (d_{002}) and d_{100}) and crystallite size from X-ray diffraction data. The estimated values are $d_{002} = 0.36$ nm (this value is higher than that of graphite of \leq 0.34 nm), and L_c = 1.43 nm. In comparison to the literature [12], $d_{002} = 0.35$ nm and $L_c = 1.38$ nm which reflects the lower surface area of our (CAC) sample. It was investigated that as d_{002} and L_c increase the surface area will decrease and vice versa [31].

FR-IR analysis

The FT-IR spectroscopy of corncob-based (AC) measured in the current study is shown in Figure 3. Characterization of corncob raw

Figure 2. XRD analysis of corncob-activated carbon (CAC)

Figure 3. FT-IR spectroscopy of corncob-based activated carbon and different

material via FT-IR is well-reported in the literature, where bands at around 1630, 1040, and 900 cm−1, in adsorption measurements, reflect the presence of cellulose and hemicellulose, while at about 1600, 1500, 1420, and 850 cm−1 are typically assigned for aromatic macromolecules [14, 32]. After activation, some of these reported bands are disappeared which could be due to the carbonization or acid treating of the corncob during the carbonization and/or activation processes. CAC sample shows a wide band at around 3480– 3100 cm−1 characterizing the adsorbed water and O–H stretching form of hexagonal groups. This wide band could also include overlapping of O–H

and N–H functional groups in their stretching vibration modes [33]. The band at about 2928 cm−1 denotes the alkyl groups with the asymmetric C–H band. The band around 1612 cm−1 attributes the C–O carbonyl groups in the stretching vibrations mode. The wide band with a peak at around 1108 cm−1 refers to C–O carbonyl groups. The peak at about 2350 cm−1 is probably not associated with activated corncob carbon which likely corresponds to the presence of minor impurity phases [28]. This findings are close to what was reported for activated corncob carbon in different treatments of several activation scenarios [14, 28, 32]. In general, the collected FT-IR data signifies that the corncob-based activated carbon is plentiful with surface functional groups.

SEM analysis

The morphology of the CAC sample is presented in Figure 4. The acid-treated corncob carbon is porous with a distorted honeycomb shape (Fig. 4a). Another morphological feature exists as tubular-like channels in which they are more likely to be associated with some sites that are only activated through the carbonization process. These tubes are connected through ellipse-shaped holes in a part of the total constitution like a grid (Fig. 4b). Thus, the morphology of CAC sample tends to have a non-homogeneou porous surface (i.e., heterogeneous surface). It can be implied that the existence of these pores and channels is due to the reaction between the HCl (2.0 M) acid and the carbon skeleton during the activation process. It can be found that tubular morphology appears in the carbonization stage of corncob material, while a clear honeycomb shape was observed after acid or alkaline activations without heating [14]. It is also observed that the acid-activated corncob carbons have high pores and heterogeneous surfaces of different sizes with different morphological shapes that can exist in the tested samples and this is agreed with Jawad et al [32].

DBT adsorption

A series of experiments were achieved to determine the best condition to accomplish the adsorption of sulfur in its form of DBT by the prepared CAC. The efficient conditions were regulated based on the removal percentage of DBT from the model crude oil (n-hexane) via the adsorption on (CAC). Figure 5 with its three panels depicts the variation of the DBT removal with (a) the contacting time (min), (b) the temperature of the mixture $(°C)$, and (c) the adsorbent dose $(g \cdot L^{-1})$. The best conditions of these values are eventually applied to the experiments of initial DBT concentration (ppm) in the n-hexane solution. The effects of these parameters will be discussed separately in the next sub-sections. For each group of tests, only one parameter was altered while the others remained constant. The constant values were 30 min, 40 °C, $3 \text{ g} \cdot L^{-1}$, and 400 ppm for time, temperature, adsorbent dose, and initial concentration of DBT.

Effect of time on DBT adsorption

The data in Figure 5a shows that the adsorption is enhanced over time. When the contacting time is 5 min the removal percent is about 72% and it slightly increases with time until it reaches about 78.5% after 20 min. Above 20 min, the percentage of DBT elimination merely rises to attain about 79% at 30 min and it almost remains constant even with increasing the contacting time to 35 min. This indicates that time has a considerable effect on the adsorption of DBT on the CAC adsorbent surface. Unfortunately, there is no reported time in the literature for removing DBT by acid-treated CAC to compare with. However, the required time to reach equilibrium with the used DBT concentration of 400 ppm and the adsorbent

Figure 4. SEM of corncob-based activated carbon treated with HCl (2.0 M)

Figure 5. Variation of DBT removal with different parameters of (a) time, (b) temperature ($\rm{^{\circ}C}$), and (c) adsorbent dose (g L⁻¹)

CAC of 3 gL^{-1} at 40 °C is relatively short (i.e., only 30 min). This time was enough for DBT molecules to be adsorbed on the outer surface and properly penetrate to some deeper active pore sites of the CAC interior surface, where the maximum removal was only 79%. Thus, 30 min is selected to be the best contact time.

Effect of temperature on DBT adsorption

Temperature is projected to present a substantial influence on DBT adsorption. The investigated temperature for adsorption of DBT on CAC is 30–70 °C with a constant initial DBT concentration of 400 ppm, time 30 min, and adsorbent dose $3 \text{ g} \cdot L^{-1}$ as shown in Figure 5b. The removal of the DBT is around 78.5% at 30 °C and becomes 79% at 40 °C. This percentage increases with temperature to attain its maximum value of about 82% at 60 °C before its decline to approximately 80.5%. This observation indicates that the adsorption process of DBT onto corncob-activated carbon is favored at high temperatures extents. This behavior implies an endothermic event in the whole adsorption process and it can be relatively attributed to hard attractive forces between the adsorbent and sorbate substances at

higher temperatures [34]. It can also suggest a strong association of DBT molecules with surface functional groups of CAC which has been enhanced by increasing temperature [35]. The elevation of temperature to 60 °C has contributed to increasing the adsorption capacity of CAC further than what has been obtained at a constant temperature of 40 °C even with increasing time to 35 °C (Fig. 5a). Therefore, the temperature of 60 °C is the best temperature for adsorption conditions.

Effect of the adsorbent dose on DBT adsorption

The effect of the adsorbent dose on the removal of the DBT from the simulated crude oil was determined by using different quantities of CAC adsorbent in the solution with a range of 1–5 gL^{-1} at a constant temperature of 40 °C, time of 30 min, and DBT concentration of 400 ppm. The results are presented in Figure 5c. The removal is around 78% when the adsorbent concentration is 1 gL^{-1} and it slightly increases with the increase of the adsorbent dose to reach about 79% at the adsorbent dose value of 3 gL^{-1} . Above that, there is no notable increase in the percentage of removal until the end of our adsorbent dose extent of 5 gL^{-1} . Thus, 3 gL^{-1} was selected as the best concentration of the absorbent substance.

Effectiveness of the best condition in adsorption of different DBT concentrations

The data in Table 1 reflects the adsorption of DBT onto corncob-activated carbon at different initial concentrations of sorbate. The initial DBT concentration varies with an extent of 100–400 ppm, while the time, temperature, and adsorbent dose are constant as they were selected to be the best conditions. From Table 1, the removal of DBT increases with the decrease of the DBT initial concentration. It is around 88% when the DBT concentration is only 100 ppm, while it gradually decreases to attain less than 83% at an initial concentration of 400 ppm which is the same as the maximum value that we obtained via the determination of the best conditions including the error of about 2%. To compare with the recently reported results of sulfur removal from naphtha (carbon and sulfur contents are close to the n-hexane) by oxidative and adsorption desulfurization techniques, the removal was less than 80% in the best conditions [5, 36]. The activity of the CAC surface and the initial concentration of DBT in the solution play a remarkable role as a driving force for DBT mass transfer between the solid and aqueous phases. The resistance to this force increases when the concentration of the DBT is above the equilibrium range. This driving force could be enhanced by temperature and the CAC concentration taking into account the effect equilibrium. For a better understanding and interpretation of the absorption

phenomenon of DBT onto CAC by utilizing the certain best conditions, we could examine the adsorption performance with particular equilibrium adsorption models as will be discussed in the next section.

Adsorption isotherm

Adsorption isotherm was employed to describe the interaction of adsorbent and adsorbate and the equilibrium distribution of DBT molecules at the solid-liquid phases [37]. Determination of the adsorption equilibrium was carried out by plotting the DBT adsorbed q_e (mg·g⁻¹), versus the DBT concentration, C_e (mg·L⁻¹) at equilibrium conditions. The equilibrium data was evaluated via the linear forms of Langmuir and Freundlich as presented in Equations 1 and 2. The linear plots of the Langmuir and Freundlich, models are shown in Figure 6a and 6b respectively, and their linking isotherms are presented in Table 2.

From Figure 6 and Table 2, the Freundlich model fits the experimental data better than the Langmuir one. This result is presented through the higher correlation factor (R^2) value for the Freundlich model of 0.9999 compared with the Langmuir of 0.9775. The isotherm directs the existence of adsorption with multilayer heterogeneous surfaces with diverse adsorption sites [38]. These findings are consistent with SEM characterization data (section 3.1.4). The value of $(1/n)$ < 1 implies strong adsorption bonds between

Time (min)	Temperature (°C)	Adsorbent dose $(g \cdot L^{-1})$	Initial DBT conc. (ppm)	Removal of DBT (%)
30	60		100	87.9 ± 1.76
30	60		200	85.8 ± 1.71
30	60		300	84.2 ± 1.68
30	60		400	82.9 ± 1.65

Table 1. Examination of the best conditions of time, temperature, and adsorbent dose

Figure 6. Adsorption data of DBT on the CAC, with best-fit of (a) Langmuir, and (b) Freundlich models

Table 2. Parameters of the Langmuir and Freundlich linear isotherm models for DBT adsorption on corncob-based AC surface at 60 °C

the DBT molecules and CAC particles due to their high intermolecular attraction within the CAC surface layers [39]. Furthermore, the value of $n > 1$ is assigned that the adsorption capacity is at satisfactory levels [40]. The maximum capacity of the monolayer adsorption of DBT onto the surface of CAC at equilibrium calculated via Langmuir simulation is 833.33 mg·g⁻¹ at 60 °C in which the removal percentage of DBT from the simulated crude oil is more than 83%. This indicates that CAC adsorbent could be a promising renewable and low-cost biomaterial for removing the undesired sulfur contents in crude oil or its light cuts.

CONCLUSIONS

The current work indicates that the activation of the carbonized corncob waste by HCl acid produces an efficient and low-cost adsorbent material for eliminating DBT from simulated crude oil (n-hexane). The carbonization and acid activation treatments contributed to a relatively high surface area and porous structure with non-homogeneous and differentshaped pores. The removal of DBT attained around 83% at examined conditions of time, temperature, and adsorption dose. Freundlich model has fitted the adsorption tests at equilibrium. The maximum adsorption capacity (qmax) calculated from nonlinear Langmuir isotherm was 833 mg·g^{-1} . The data indicated that CAC is an effective adsorbent for the adsorption of dibenzothiophene (DBT).

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