Breakthrough curves of oil adsorption on novel amorphous carbon thin film

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ABSTRACT

A novel amorphous carbon thin film (ACTF) was prepared by hydrolyzing wood sawdust and delignifying the residue to obtain cellulose mass that was subjected to react with cobalt silicate nanoparticle as a catalyst under the influence of sudden concentrated sulfuric acid addition at 23 °C. The novel ACTF was obtained in the form of thin films like graphene sheets having winding surface. The prepared ACTF was characterized by Fourier-transform infrared spectrometer, transmission electron microscope (TEM), and Brunauer–Emmett–Teller (BET). The adsorption capacity of ACTF to remove oil from synthetic produced water was evaluated using the incorporation of Thomas and Yoon–Nelson models. The performance study is described through the breakthrough curves concept under relevant operating conditions such as column bed heights (3.8, 5 and 11 mm) and flow rate (0.5, 1 and 1.5 mL.min⁻¹). It was found that the oil uptake mechanism is favoring higher bed height. Also, the highest bed capacity of 700 mg oil/g ACTF was achieved at 5 mm bed height, and 0.5 mL.min⁻¹ flow rate. The results of breakthrough curve for oil adsorption was best described using the Yoon–Nelson model. Finally, the results illustrate that ACTF could be utilized effectively for oil removal from synthetic produced water in a fixed-bed column system.

Key words | breakthrough curve, novel amorphous carbon thin film, oil adsorption, produced water treatment, Thomas and Yoon–Nelson models, wood sawdust

INTRODUCTION

Activated carbon, called activated charcoal, activated coal, carboactivatus or an ‘AC filter’, is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reactions. Activated is sometimes substituted with active, due to its high degree of microporosity; just one gram of activated carbon has a surface area in excess of 500 m², as determined by gas adsorption (Jhadhav 2015).

Adsorption on activated carbon structures is caused by London Dispersion Forces, a type of Van der Waals Force which exists between molecules. The force acts in a similar way to gravitational forces between planets. London Dispersion Forces are extremely short range and therefore sensitive to the distance between the carbon surface and the adsorbate molecule (Wohleber & Manes 1971; Manes & Greenbank 1983; Greenbank & Manes 1984). They are also additive, meaning the adsorption force is the sum of all interactions between all the atoms. The short range and additive nature of these forces results in activated carbon having the strongest physical adsorption forces of any material known to mankind. Liquid phase adsorption can be described by the molecules exiting from the mass phase of being absorbed in the pores in a semi-liquid state. The driving force for adsorption is the proportion of the concentration to the solubility of the compound (Cychoz et al. 2008).

Prediction of breakthrough curve for a fixed bed through a sophisticated mass-transfer model needs many parameters that must be determined by independent batch kinetic study or estimated by suitable correlations (Pan et al. 2005). Therefore, the simplified method was developed using one lumped parameter to predict the breakthrough times of fixed-bed adsorption processes that can be applied for predicting the breakthrough curve in low concentration ranges (Xiu & Li 2000; Rengaraj & Yeon 2001; Zhang & Chung 2001; Grand & Otero 2004). The effects of the flow rate and bed height on the breakthrough curves was investigated by Sherwood & Pigford (1975), Chern & Chien (2002), Li et al. (2002), Chang et al. (2006) and Purnomo & Prasetya (2007).
This research aimed to prepare novel amorphous carbon thin film (ACTF) in the form of thin films like graphene sheets having a winding surface; in this respect the cellulose mass obtained from pre-treated wood sawdust (WD) reacts with cobalt silicate nanoparticle as a catalyst under the influence of sudden addition of concentrated sulfuric acid at 23 °C, such a method being called a catalytic acid spray method. The performance of novel ACTF to adsorb oil from synthetic produced water using a fixed bed sorption system was examined. The effects of the flow rate and bed depth on the breakthrough curves will be investigated at high concentration ranges. The breakthrough curves of ACTF were predicted using Thomas and Yoon–Nelson models.

**EXPERIMENTAL**

**Materials**

WD was collected from local workshops of the furniture trade in Egypt. The collected WD chemomaterial was washed with hot deionized water, dried in a hot air oven at 333 K to a constant weight, crushed with a grinder, sieved to constant sizes (0.1–0.07 mm), then stored in a tight bottle until used. Synthetic produced water–oil mixture was prepared using Egyptian condensate oil at a concentration of 1,000 mg/L with a density of 0.7928 mg/L; the prepared oil–water emulsion was stable for 30 days at droplet size ranges of 1–2 micrometers. The concentration of oil was measured by the total suspended solids method according to ASTM D 5903 standard method. Cobalt nitrate Co(NO₃)₂·6H₂O, silica, ethanol, H₂O₂ and sodium hydroxide were purchased from Sigma–Aldrich.

**Pretreatment of WD**

WD was subjected to a pretreatment process. Hence, hemicellulose was solubilized by the dilute acid hydrolysis at 120 °C for 60 min, using 1% (wt/wt) sulphuric acid, and the resulting residue subjected to the delignification process at 120 °C for 60 min using alkaline peroxide, which was a mixture of 1.5% (wt/wt) NaOH and 0.5% (wt/wt) H₂O₂.

During the dilute acid hydrolysis, the hemicellulose was solubilized in the form of monomeric sugars into the hydrolyzate, and the succeeding delignification process removed lignin and a small of silica present in the pre-treated WD into the black liquor.

**Preparation of cobalt silicate nanoparticles**

Cobalt silicate nanoparticles were prepared according to Fu et al. (2006). In this respect, 4.0 g of the freshly prepared cobalt nitrate and silica was vigorously stirred with 200 mL of ethanol for 30 min at 45 °C, then 40 mL water, and 4 mL (1.4 M) NaOH was added to the above suspension. Then the powder was separated and dried at 50 °C for 8 h in a vacuum oven.

**Preparation of amorphous carbon thin film (ACTF)**

Five grams of cellulose obtained from pre-treated WD was added to 5 mL concentrated sulfuric acid in the presence of 0.1 g silica and stirred for 10 min, then filtered and washed with hot deionized water until it reached pH 7 and kept in an oven at 40 °C for 6 h. The prepared semi-carbonized cellulose was poured into a flask in the presence of 0.01 g cobalt silicate nanoparticles and heated up to 40 °C for 30 min. The prepared ACTF was left to cool for 1 h, then dried in a vacuum oven for 24 h at 50–70 °C.

**Characterization of ACTF adsorbent**

The infrared spectra of the ACTF adsorbent before and after oil adsorption were obtained using a Fourier-transform infrared spectrometer (FTIR, model Spectrum One, Perkin Elmer, USA). The adsorbent samples were prepared as KBr pellets by gently mixing 10 mg of ACTF with 300 mg of KBr powder and compressed into discs at a force of 17 kN for 5 min using a manual tablet presser. The prepared KBr pellets were scanned over the range of 400–4,000 mm⁻¹ to identify the functional groups that were responsible for adsorption. Microstructure and surface morphology of the ACTF adsorbent before and after adsorption were examined using high resolution transmission electron microscope (HRTEM, model JEOL JEM 2200FS TEM with a field-emission gun operating at 200 kV), and scanning electron microscope (SEM, JEOL JSM 6710F). The surface area, total pore volume, and pore size distribution of the prepared ACTF adsorbent were determined by N₂ adsorption at 77 K using an Autosorb (Nova 3200, Quantachrome Corp., USA). The sample was degassed at 383–393 K overnight, prior to the N₂ adsorption experiments. The Brunauer–Emmett–Teller (BET) surface area and pore volume were obtained by applying the BET equation and p/p₀ = 0.95 to the adsorption data, respectively. The pore size distribution was derived using the density functional theory method.
Study the fixed bed adsorption

Figure 1 represents the schematic diagram of the fixed-bed adsorption system. Continuous flow adsorption studies were conducted in a column made of Pyrex glass tube having inner diameter of 0.6 and 100 mm height. A sieve made up of stainless steel was placed at the bottom of the column. Over the sieve, a layer of glass wool was placed to prevent loss of adsorbent. A peristaltic pump (model Masterflex, Cole-Parmer Instrument Co., USA) was used to pump the feed upward through the column at a desired flow rate. The solution was pumped upward to avoid channeling due to gravity (Xu et al. 2013).

Thomas model

The Thomas model is one of the most general and widely used models to describe the behavior of sorption processes in fixed-bed columns. The model is based on the assumption that the process follows Langmuir kinetics of sorption–desorption with no axial dispersion. Its main limitation is that its derivation is based on second-order kinetics and considers that sorption is not limited by the chemical reaction but controlled by the mass transfer at the interface (Thomas 1944). This discrepancy can lead to errors when this method is used to model sorption processes in specific conditions. The Thomas model has the following form:

\[
\frac{C}{C_o} = \frac{1}{1 + \exp \left( \frac{K_T q_m}{Q} C_o t \right)},
\]

also expressed as

\[
\log \left( \frac{C}{C_o} - 1 \right) = \frac{K_T q_m}{2.303Q} C_o t.
\]

where \( C, C_o \) = the effluent and inlet solute concentrations (mg/L), \( q \) = the maximum adsorption capacity (mg/g), \( m \) = the total mass of the adsorbent (g), \( Q \) = volumetric flow rate (mL.min\(^{-1}\)), and \( K_T \) = the Thomas rate constant (mL.min\(^{-1}\)/mg). The constants \( K_T \) and \( q \) can be determined from a plot of \( \log \left( \frac{C}{C_o} - 1 \right) \) against \( t \) (Ahmad & Hameed 2010; Ghribi & Chlendi 2011).

Yoon–Nelson model

This model is scientifically equal to the Thomas model, and it has additionally been applied within the oil concentrations of the effluent during the breakthrough and saturation time of the column. This model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. The linear form of the Yoon and Nelson equation regarding a single-component system is expressed as

\[
\ln \left( \frac{C}{C_o} - C \right) = K_{YN} t - \tau K_{YN}
\]

where \( K_{YN} \) is the rate constant of the model, \( \tau \) is the time for 50% breakthrough oil and \( t \) is the breakthrough time. The \( K_{YN} \) and \( \tau \) are determined from a plot of \( \ln \left( \frac{C}{C_o} - C \right) \) against sampling time (\( t \)). The derivation of Equation (3) is based on the definition that 50% breakthrough oil occurs at \( t = \tau \). Thus, the fixed bed of ACTF should be completely saturated at \( t = 2\tau \). According to the symmetrical nature of breakthrough curves of the Yoon–Nelson model, the amount of oil being adsorbed in the fixed bed is half of the initial oil concentration path through the fixed bed within \( 2\tau \) period (Yoon & Nelson 1984). Consequently, the following equation can be expressed as a
given bed:

\[ qYN = qtotM = (12C0(Q1000)(2t)M = C0Qr1000M \]  \hspace{1cm} (4)

This equation also enables determination of the adsorption capacity of the column \( qYN \), initial oil concentration \( C_0 \), flow rate \( Q \), chemomass quantity in the column \( M \) and 50% breakthrough time \( t \) by using the Yoon–Nelson model (Bharrathi et al. 2011).

RESULT AND DISCUSSION

Characterization of the ACTF adsorbent

The characterization of the ACTF adsorbent included FTIR analysis, SEM analysis and textural properties identification (BET analysis).

FTIR analysis

The identification of the chemical structure of ACTF before and after oil adsorption could verify the possible functional groups involved in adsorption processes. Figure 2 depicts the FTIR spectra of WD and ACTF before and after oil adsorption. All these spectra exhibit a strong band at 3,650–3,445 cm\(^{-1}\) that is attributed to the intra- and inter-molecular hydrogen-bonded (O-H) stretching that occurs in cellulose of WD and also in water molecules adsorbed on the surface of ACTF. The broad peaks at approximately 1,110, 1,060 and 1,035 cm\(^{-1}\) show the C-O-C stretching vibration of lignin and the C-O stretching of cellulose and hemicelluloses in WD, which disappeared in ACTF. ACTF-Oil spectra are characterized by the presence of a peak observed at 1,730–1,705 cm\(^{-1}\) attributed to stretching carbonyl groups C=O, and the two peaks observed between 2,920 and 2,850 cm\(^{-1}\) were described as asymmetric and symmetric stretching of vibration of methylene C-H adsorption bands originating from the alkyl chain in ACTF after oil adsorption, which revealed a good adsorption of oil onto the ACTF adsorbent under study. In addition to presence of the stretching vibration, a peak of the C=C was observed in the range of 1,650–1,505 cm\(^{-1}\), which may be attributed to the aromatic ring after oil adsorption. The bands at 1,460–1,450 cm\(^{-1}\) and 1,420–1,400 cm\(^{-1}\) may represent CH\(_3\) and CH\(_2\) asymmetric deformation. The band at 1,380–1,375 cm\(^{-1}\) represents CH\(_3\) symmetric deformation.

SEM and HRTEM analysis

Furthermore, SEM and HRTEM were used to characterize the surface morphologies, where surface roughness with a suitable microstructure can affect the oil adsorption capacity of the adsorbent. Figure 3(a) and 3(b) show the SEM images of WD sample and ACTF adsorbent after oil adsorption, and Figure 3(c) shows the TEM of ACTF prepared. It can be observed from Figure 3(a) that

![Figure 2](https://iwaponline.com/wst/article-pdf/73/10/2361/461488/wst073102361.pdf)
the surface of WD gives cross-interconnected pores. The SEM image of ACTF after oil adsorption indicates that the pores of ACTF were filled and adhered with oil, which covered the surface of the adsorbent with a series of irregular oil cavities, as shown in Figure 3(b). Irregular surfaces implied the adsorption of oil on the ACTF adsorbent. Figure 3(c) illustrates that ACTF is prepared in the form of thin films like graphene sheets, and this image is significantly similar to graphene sheets prepared from graphite or by any other method. This illustrates that ACTF consists of many accumulated sheets, and their numbers during the preparation process can be controlled. In the future we will try to modify the preparation process to be more highly precise for given superiority results.

**Textural properties identification (BET analysis)**

Moreover, the physical parameters obtained from N$_2$ adsorption isotherm, including surface area, total pore volume, and pore size distribution of the studied WD and the prepared ACTF samples are given in Table 1. It is evident that the surface area and pore volume of ACTF was greater by approximately 2.5 times and 3.5 times, respectively, than that of WD. This possibly enhances the ability of the adsorbent for trapping oil and facilitates the pore distribution during adsorption. Also, the average pore size increased from 2.75 Å to 3.89 Å. Overall, the BET analysis shows significant increase in the surface area, pore volume and pore diameters on treatment of WD and preparation of ACTF.

**Column studies**

**Effect of bed height**

To study the breakthrough curve for oil adsorption on ACTF, three different bed heights of ACTF, 3.8, 5 and 11 mm, have been used, as shown in Figure 4(a) and 4(b). It is noticeable from Figure 4(a) that the bed height 5 mm takes longer time than 3.8 and 11 mm to remove oil from produced water. Hence, the breakthrough point of bed height 5 mm started at 100 min later than the corresponding bed height 3.8 and 11 mm, which explains how large a water volume has been treated using the bed height 5 mm. Figure 4(b) shows that the bed height 5 mm takes up the largest volume of produced water, as confirmed by Figure 4(a). Although the numbers of active sites on the ACTF surface increases, the effect of bed
height on the oil removal is not effective to remove oil from produced water. This is verifying the effectiveness of ACTF to remove oil simultaneously with salts, containing poly and divalent cations (Ca$^{2+}$, Mg$^{2+}$), as verified previously from Figure 4(a) and 4(b).

Effect of flow rate

Flow rate is an important parameter in evaluating the performance of a chemosorption process, particularly for continuous treatment of wastewater on an industrial scale. The effect of flow rate on oil adsorption is shown in Figure 5.

### Table 2

<table>
<thead>
<tr>
<th>Flow (mL/min)</th>
<th>$k_T$</th>
<th>$R^2$</th>
<th>$q_{(mg/L)}$</th>
<th>$q_{(mg/g)}$</th>
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<tr>
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<td>0.996987</td>
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<td>1</td>
<td>0.00043</td>
<td>0.99636</td>
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<td>0.00046</td>
<td>0.98794</td>
<td>300</td>
<td>999.488</td>
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![Figure 4](https://iwaponline.com/wst/article-pdf/73/10/2361/461488/wst073102361.pdf) Effect of bed height of oil adsorption on ACTF.

![Figure 5](https://iwaponline.com/wst/article-pdf/73/10/2361/461488/wst073102361.pdf) Effect of flow rate of oil adsorption on ACTF.

![Figure 6](https://iwaponline.com/wst/article-pdf/73/10/2361/461488/wst073102361.pdf) Effect of bed height of regeneration process on oil adsorbed.
scale. Therefore, the effect of flow rate on chemosorption of oil by ACTF was studied by varying the flow rates from 0.5 to 1 and 1.5 mL.min\(^{-1}\) at initial oil concentration of 1,000 mg/L and bed height of 5 mm. At the above flow rate conditions, the breakthrough performance for oil adsorption on ACTF is represented in Figure 5(a) and 5(b). In the breakthrough time Figure 5(a), the chemosorption efficiency of ACTF was lower at higher flow rate. As the flow rate was increased, the breakthrough time decreased through 2 h. This is due to the fact that at higher flow rate the contact time is decreased, because the oil droplets do not have enough time to capture the binding sites on ACTF surface or diffuse into its pores. Figure 5(a) depicts the breakthrough time. It is obvious that when the breakthrough curve became steeper as the flow rate increased, the oil removal efficiency decreased. When the flow rates decrease, the external mass transfer controls the oil adsorption process and the system is ideal for intra particle diffusion. Thus, at lower flow rates (0.5 mL.min\(^{-1}\)), the diffusion process will be more effective and the residence time of the adsorbate is higher; consequently, a high sorption capacity will result, as shown in Figure 5(a) and 5(b).

Regeneration process

The regeneration process of oil adsorbed on activated carbon thin film studied at different bed heights of 3.8, 5 and 11 mm, at 0.5 mL.min\(^{-1}\) flow rate using n-hexane. There was found a large degree of similarity between the oil removed from ACTF and its ability to adsorb oil for a long time and with large volumes up to 50 times as much as the volume of the ACTF. The regeneration process showed the ability of ACTF to maintain its electronic structure and active sites and carboxylic groups on its surface for a long time, and this confirmed the chemical stability of ACTF as shown in Figure 6.

Kinetic study of Thomas model

The sorption data at three different flow rates of 0.5, 1 and 1.5 mL.min\(^{-1}\) at an initial oil concentration of 1,000 mg/L and bed height of 5 mm for the sorption systems of oil by ACTF were applied using the Thomas model. The Thomas rate constant (\(k_T\) (slope) and the bed capacity (the intercept) are calculated from the plot of \(\ln \frac{C}{C_0} - 1\) versus \(t\) at different flow rates as shown in Figure 7. Values of \(k_T\) and \(q_0\) along with the regression coefficients are presented in Table 2. \(R^2\) values of 0.996987, 0.99636 and 0.98794 under the operating conditions suggested that the Thomas model was suitable for describing the chemosorption of oil on ACTF. From Table 2, at a constant depth of 5 mm, as the flow rate increased from 0.5 to 1.5 mL.min\(^{-1}\) the maximum oil chemosorption capacity increased from 177 to 999 mg/g. From Figure 7, it is clear that there is a good agreement between the experimental points and model predicted values. The correlation factor error between the experimental data and those calculated from the model is ±0.4.

<table>
<thead>
<tr>
<th>(T_{(exp.)})</th>
<th>Flow (ml.min(^{-1}))</th>
<th>(K_{YN})</th>
<th>(R^2)</th>
<th>(T_{(theo.)})</th>
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<td>1.5</td>
<td>0.00082</td>
<td>1</td>
<td>327.663</td>
</tr>
</tbody>
</table>
Kinetic study of Yoon–Nelson model

The Yoon–Nelson model was also applied to the column data obtained from chemosorption by ACTF, and the Yoon–Nelson constant \(k_{YN}\) and \(\tau\) (the time required for 80% adsorbate breakthrough) were determined from the plot of \(\ln \left(\frac{C}{C_0-C}\right)\) versus time. Table 3 represented the value of these calculated parameters. The experimental data exhibited good fit to the Yoon–Nelson model, with \(R^2\) that recorded 0.99416, 0.96269 and 1, which was better than its corresponding value with Thomas model in both cases – chemosorption and physisorption of oil by ACTF. The bed capacity was found to increase with the increase in flow rate in the chemosorption of oil by ACTF. The comparison of the experimental and predicted breakthrough curves obtained in the chemosorption of oil by ACTF at different flow rates (0.5 mL.min\(^{-1}\), 1 mL.min\(^{-1}\) and 1.5 mL.min\(^{-1}\)) at a constant bed height (5 mm) according to the Yoon–Nelson model is shown in Figure 8. From the figure, it is clear that there was a good agreement between the experimental points and model predicted values.

CONCLUSIONS

In this study the ACTF was synthesized from WD to adsorb oil from synthetic produced water using a fixed bed sorption system. The prepared ACTF was verified before and after oil adsorption using FTIR, SEM, HRTEM and BET analysis. The ability of prepared ACTF for trapping oil was verified through breakthrough curves using Thomas and Yoon–Nelson models to predict the relationship between bed height and flow rate using column process design. The uptake capacity of ACTF increases with increasing bed height and decreases with increasing flow rate. A maximum uptake of 700 mg oil/g adsorbent was achieved at 5 mm bed height and 0.5 mL.min\(^{-1}\) flow rate. The experimental data fitted both the Thomas and Yoon–Nelson models, but the Yoon–Nelson model is a better description of the experimental kinetic data than the Thomas model. It was observed that the adsorption cycle took 2 h, after which the adsorption process reached the equilibrium stage.

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