Modeling Hydrogen Sulfide Adsorption by Activated Carbon made from Anaerobic Digestion By-Product

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
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University of Toronto

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Abstract

Biogas, produced from anaerobic digestion of cattle manure, is an attractive alternative energy source as it is rich in methane. However, it is necessary to remove hydrogen sulfide from the biogas before it can be used in engines for electricity generation. Currently, large scale biogas systems employ physical adsorbing solvents to upgrade and purify biogas which is not economically feasible for small scale biogas systems. Activated carbon made from anaerobic digestate proves to be an effective adsorbent of hydrogen sulfide because it has minimal operating costs and essentially zero raw material cost. A model is developed to predict the adsorption capacity, carbon bed life span, and breakthrough time for this carbon material. By analyzing the reaction constant, adsorption constant, and degradation constant, adsorption behavior under different operating conditions were studied. The model can be scaled-up to model adsorption for biogas loading rates for small to large scale cattle farms.
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Chapter 1
Introduction

1 Introduction

1.1 Overview

Over the decades, more and more interest has been focused on finding alternative energy sources to reduce our reliance on petroleum based energy. The push towards these initiatives stem from the need to find environmentally sustainable sources and the need to mitigate the foretold global energy crisis. Biogas, produced from anaerobic digestion of organic material, is rich in methane and can be combusted for heat and/or electricity. Biogas is composed of 40-70% methane, 60-30% carbon dioxide, and 100-3000ppmv hydrogen sulfide. Biogas is produced through the anaerobic digestion of various feedstock, such as animal manures, food wastes, municipal wastewater sludge, and crop residue. However, it is necessary to remove hydrogen sulfide from the biogas before it can be used in engines as hydrogen sulfide causes equipment corrosion and the formation of sulfur oxides when combusted. Currently, large scale biogas systems employ physical adsorbing solvent to upgrade (remove carbon dioxide) and purify (remove hydrogen sulfide) biogas. However, this process is not economically feasible for small scale biogas systems.

In particular, this project focuses on the potential to develop an economical and easy to operate unit to remove hydrogen sulfide for small, medium and large cattle farms. Only the purification step is required as the removal of carbon dioxide is not necessary for stationary engine-generators or to produce electricity. In previous work by White (White, 2010), activated carbon made from anaerobic digestate proved to be an effective adsorbent of hydrogen sulfide which had minimal operating costs, and zero cost for raw material as the carbon was made from manure digestate. Therefore, if biogas can be purified economically from cattle farms, it is a very attractive alternative energy source as there are many untapped resources available.

1.2 Objectives

The objective of this thesis is to develop a model for the adsorption of hydrogen sulfide on activated carbon made from anaerobic digestion by-product. This model is used to study the
mechanisms and behavior of hydrogen sulfide adsorption on the activated carbon. The model will be used to predict the bed adsorptive capacity, breakthrough time, carbon bed life span. The model can also be used for scale-up and design.

1.3 Thesis Outline

There are seven chapters in this paper. The first chapter is an introduction to the purpose of the work completed and relates to prior work that has been done on this specific project. The second chapter is a literature review of hydrogen sulfide adsorption on activated carbon. The third chapter explores different adsorber models and solutions; each model is fitted to experimental data and analyzed. Chapter 4 relates the different model parameters to adsorption mechanisms and adsorption behaviors. In Chapter 5 a sensitivity analysis of different operating parameters on the effect of adsorption behavior is done. In Chapter 6 a scale-up and capital cost estimate of the unit is completed. Lastly, in Chapter 7 is a summary of the overall conclusions and future work to be completed.

1.4 Prior Work

All experimental work was conducted by Andrew White and documented in his Master of Applied Science thesis, completed at the Department of Chemical Engineering and Applied Chemistry, University of Toronto 2010. The activated carbon samples were prepared by White and then used as an adsorbent in a fixed bed adsorber. White optimized the parameters in which the carbon was pyrolysed and activated, to obtain an activated carbon that had high adsorptive capacity. The experimental data collected from the adsorber bed was analyzed for adsorption capacity for each sample of carbon prepared. Characterization of the raw materials and activated carbon produced was also completed in previous work to define the inorganic components of the carbon, the pH of the carbon surface, the surface area and pore volume, as well as XPS analysis. White also completed a full economic analysis on the feasibility of the project. As such, this analysis will not be repeated in this thesis, however, the capital cost of the unit will be estimated in Chapter 6 providing new information.
Chapter 2
Literature Review

2 Literature Review

2.1 Introduction

Hydrogen sulfide is an unwanted pollutant that can be found in many industrial gas waste streams in concentrations that are of environmental and health concern. It is important to remove hydrogen sulfide from gas streams for many reasons such as meeting product purity requirements, generating clean fuels, preventing environmental pollution causing health problems, and to avoid catalyst poisoning and corrosion in gas processing units (Wang, 2003). Moreover, more stringent environmental policies have been administered by governmental organizations, such as the U.S Environmental Protection Agency, which demands that desulfurization is necessary before releasing the gas stream to the atmosphere (Savage, 1976) (Bagreev & Bandom, 2001). Currently in industry, the Claus process, which is a direct conversion process, is the most widely employed method for the removal of hydrogen sulfide (Kirk-Othmer, 1999-2011). Though the removal efficiency of this process is over 99% conversion, it is both energy and cost intensive (Syed, Soreanu, Falletta, & Beland, 2006). Furthermore, at concentrations below 10%v/v, the Claus process is not economical (Grekel, 1959) (Steijns & Mars, 1977) and adsorption or oxidation to sulfur oxides is preferred. As such, many alternative methods have been suggested for the removal of hydrogen sulfide. These alternatives include adsorption-reaction processes and biological processes.

Molecular sieves, silica gel, and activated carbons have been used to successfully adsorb hydrogen sulfide from waste gas streams (Meeyoo, Lee, Trimm, & Cant, 1998). Molecular sieves were found to have the highest capacity for hydrogen sulfide removal under dry conditions (Tanada & Boki, 1974), but their effectiveness decreased significantly for wet streams (Meeyoo, Trimm, & Cant, 1997). Whereas, activated carbons showed good adsorption capacity for both dry and wet streams (Meeyoo, Trimm, & Cant, 1997). Activated carbons are known to be very good adsorbents and have been previously employed in many processes such as filtration, purification and deodorization (Meljac, Perier-Camby, & Thomas, 2005). They are widely available, and are relatively inexpensive materials in comparison to other inorganic
adsorbents such as zeolites, alumina and silica (Xiao, Wang, Wu, & Yuan, 2008). Many chemical groups such as red-ox and acid-base couples resulting from activation processes are distributed on the activated carbon surface (Meljac, Perier-Camby, & Thomas, 2005). The surface chemistry of the activated carbon allows for direct oxidation of hydrogen sulfide via the following reaction (Ghosh & Tollefson, 1986):

\[
H_2S + \frac{1}{2}O_2 \rightarrow \frac{1}{x}S_x + H_2O \quad (2.1)
\]

\[\Delta H = -206.4 \text{ kJ/mol}\]

In an undesired side reaction, a small quantity of hydrogen sulfide is converted to sulfur dioxide via oxidation reaction (Savage, 1976) with the sulfur produced in reaction (Wang, 2003). The selectivity for the side reaction ranges from 3-6% depending on the organic precursor (Dalai, Cundall, & De, 2008).

\[
S + O_2 \rightarrow SO_2 \quad (2.2)
\]

2.2 Activated Carbon Characteristics

The specific characteristics, physical and chemical properties of activated carbons, depend on both organic precursor and activation processes (Meljac, Perier-Camby, & Thomas, 2005). Activated carbons are advantageous as adsorbents and catalyst supports because they offer high surface area, developed pore volume, unique surface properties and the opportunities for surface chemistry modification (Xiao, Wang, Wu, & Yuan, 2008). Activated carbon materials have random cross-linked networks, which provide highly developed and accessible internal pore structures pertinent to the adsorption of contaminants (Dalai, Cundall, & De, 2008).

It was observed by Bandosz (Bandosz T. J., 2006) and Feng et al. (Feng, Kwon, Borguet, & Vidic, 2005) that carbon particles with both micropores and mesopores provided greater removal efficiency than microporous particles with higher surface area. Mesoporosity allows for a higher diffusion rate of hydrogen sulfide to the active sites and also enhances the deposition of sulfur product (Dalai, Cundall, & De, 2008). Mesopore structure is important for prolonged carbon life activity, as larger pores (>100nm) are not as easily blocked by sulfur buildup whereas small
pores are. Once a pore is blocked, the active sites become unavailable; with larger pores molten sulfur can drop from the surface thereby renewing the active sites (Dalai, Cundall, & De, 2008).

The activation of the organic precursor consists of two steps: carbonization and activation. During carbonization, volatile organic components are eliminated and the carbon structure rearranges into graphite sheets laid out random order (Meljac, Perier-Camby, & Thomas, 2005). After carbonization, the carbonaceous skeleton obtained has a significant internal porosity. During activation, an oxidizing agent attacks the carbons located at the edges of the graphitic sheets, resulting in the pores being opened and widened to create the desired micro and mesopore structure (Meljac, Perier-Camby, & Thomas, 2005). Below is a table of data collected by Bandosz (Bandosz T., 1999), which compares the surface area and pore volume distribution of different types of activated carbon.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET} (m^2/g)$</th>
<th>$V_{tot} (cm^3/g)$</th>
<th>$V_{micro} (cm^3/g)$</th>
<th>$V_{&lt;5Å} (cm^3/g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>1700</td>
<td>1.18</td>
<td>0.410</td>
<td>0.004</td>
</tr>
<tr>
<td>M</td>
<td>2240</td>
<td>0.98</td>
<td>0.609</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>1040</td>
<td>0.49</td>
<td>0.361</td>
<td>0.19</td>
</tr>
</tbody>
</table>

There are two main methods, physical and chemical, by which the organic precursors are activated. Chemical activation employs an oxidizing agent which are normally alkali and alkaline earth metals or acids such as KOH, K$_2$CO$_3$, NaOH, Na$_2$CO$_3$, AlCl$_3$, ZnCl$_2$, MgCl$_2$ and H$_3$PO$_4$, (Bansal, Donnet, & Stoeckli, 1988) (Otowa, Nojima, & Miyazaki, 1997) (Jagtoyen & Derbyshire, 1998) (Tsai, Jeng, & Chiang, 2002). The oxidizing agent is mixed with the precursor material and heated at high temperature (600-1000°C), resulting in simultaneous carbonization and activation (Meljac, Perier-Camby, & Thomas, 2005). Although, washing treatments are carried out after activation/carbonization, the oxidizing agent still lingers on the carbon surface and changes its surface chemistry. In physical activation, the carbon material is carbonized at high temperature before undergoing reactions in the gaseous phase with CO$_2$, or steam (Tsai,
Jeng, & Chiang, 2002). Physical activation is more expensive, but the final product is clear of chemical additives.

Heteroatoms such as oxygen, nitrogen, hydrogen and phosphorus are functional groups that can be found on the activated carbon surface (Puri, 1970) (Leon y Leon & Radovic, 1992) (Boehm, 1966). Hydrogen and nitrogen originate from the precursor material, oxygen is introduced via a chemisorption process when carbon is exposed to air, and phosphorus is introduced via chemical activation with oxidizing agents (Bandosz T. J., 2001). These species impact the adsorption capacity of the material since they change the pH of the surface. Functional groups are responsible for the physisorption onto the pore surface due to van der Waals forces, and chemisorption by forming hydrogen bonds; which are the two adsorption phenomena that occur during hydrogen sulfur adsorption (Guo, et al., 2007). Below is a table obtained from Bandosz (Bandosz T., 1999) that shows the surface functional group content in different types of activated carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH of Carbon Suspension</th>
<th>H₂S capacity at breakthrough (g/cm³)</th>
<th>H₂S capacity at breakthrough (g/g)</th>
<th>Sulfur content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>6.2</td>
<td>0.014</td>
<td>0.047</td>
<td>0.40</td>
</tr>
<tr>
<td>M</td>
<td>7.6</td>
<td>0.003</td>
<td>0.012</td>
<td>0.32</td>
</tr>
<tr>
<td>C</td>
<td>7.7</td>
<td>0.003</td>
<td>0.009</td>
<td>0.72</td>
</tr>
</tbody>
</table>

2.3 The Effect of Temperature

The desired operating temperature range would be between the dew point temperature (125°C) and boiling point temperature (200°C) of sulfur, so that molten sulfur will flow down the reactor bed. For both impregnated and virgin carbon, it was found that as temperature increased within the range of 125-175°C, the removal efficiency increased dramatically. However, in the 175-200°C range, very little improvement was observed (Dalai, Cundall, & De, 2008).
For impregnated carbons, it was observed that an increase in temperature resulted in breakthrough capacity being achieved faster and equilibrium adsorption capacity decreased slightly. Higher temperatures would probably enhance physisorption but was disadvantageous for chemical adsorption (Xiao, Wang, Wu, & Yuan, 2008).

2.4 The Effect of Relative Humidity

Under dry conditions, a rapid breakthrough was observed and the outlet concentration increased rapidly as process time progressed. It can also be seen that breakthrough time was delayed with increased relative humidity (Bagreev & Bandosz, 2001) (Bandosz T. J., 2001) (Bouzaza, Laplanche, & Marstea, 2004). It can be concluded that water plays a key role in the H₂S adsorption process. When humidity is high, a sufficient amount of water is adsorbed and capillary condensation of water vapor takes place in the pores of activated carbons (Bouzaza, Laplanche, & Marstea, 2004). A water film is thus formed on the internal surface of activated carbon. It was proposed that the molecules of hydrogen sulfide are transported and dissolved to produce H⁺ and HS⁻ ions into the water film (Bouzaza, Laplanche, & Marstea, 2004). The role of water is found to be more than just a solvent, as tests were run with methanol and decanol as solvents, of which hydrogen sulfide is more soluble in, and no chemical reaction was achieved (Meeyoo, Lee, Trimm, & Cant, 1998).

The presence of water has a beneficial effect on the adsorption performance of H₂S on both impregnated and unmodified activated carbon. There are two reason hypothesized for this behavior:

i) the catalytic reaction may take place in the water phase (which is faster than directly on the carbon surface) within the pores of the catalyst by dissolving oxygen and hydrogen sulfide in the water film formed (Pimavera, Tro Farelli, Audreussi, & Dolcetti, 1998)

ii) the presence of water slows down the degeneration process of the activated carbon by promoting deposition of sulfur by mechanically removing sulfur from the active sites (Pimavera, Tro Farelli, Audreussi, & Dolcetti, 1998)
2.5 The Effect of Gas Composition

Under dry conditions, in 100% nitrogen atmosphere, it was shown that hydrogen sulfide can be oxidized on activated carbon. This proves that the carbon material is able to oxidize sulfur compounds without the presence of oxygen in the feed gas. The oxidation capacity of the carbon material is due to the oxygen functional groups found on its surface (Bouzaza, Laplanche, & Marstea, 2004). The presence of oxygen and carbon dioxide leads to slower kinetics than under pure nitrogen conditions.

Under humid conditions, the opposite effects are observed. Under nitrogen atmosphere, the hydrogen sulfide degradation kinetics is hypothesized to be limited by oxygen disposal (Bouzaza, Laplanche, & Marstea, 2004). The role of the humidity proves to be highly advantageous for the degradation of hydrogen sulfide when the gas phase is carbon dioxide or oxygen. The acidification of the carbon surface due to the presence of water is largely counterbalanced by the dissolution of the acidic products formed (Bouzaza, Laplanche, & Marstea, 2004). The degradation kinetic is improved even if an acidification of the surface occurs since the dissolution of the by-products in the water film permit regeneration of the active sites. (Bouzaza, Laplanche, & Marstea, 2004)

Important factors when comparing gas composition:

- The effect of humidity is negligible under a nitrogen atmosphere. The kinetics are limited by the accessibility of the active sites by hydrogen sulfide or the disposability of oxygen (Bouzaza, Laplanche, & Marstea, 2004).

- The influence of relative humidity is important when carbon dioxide is present. The water seems to play a role in dissolving the acidic by-products which leads to an easier access for hydrogen sulfide to the active sites (Bouzaza, Laplanche, & Marstea, 2004).

- In the presence of oxygen, the effect of water is effective during the beginning of the reaction. This could be due to the increased solubility of hydrogen sulfide and oxygen, and then the reaction happens in the liquid phase. Or another hypothesis is that in the water phase, the oxidation of hydrogen sulfide leads to the formation of sulfuric acid and the two radicals $\text{OH}^-$ and $\text{O}_2^-$. These radicals react with the hydrogen sulfide and accelerate the oxidation reaction (Bouzaza, Laplanche, & Marstea, 2004).
2.6 Impregnated Carbons

Since hydrogen sulfide is acidic, a caustic carbon surface would help immobilize the species on the adsorbent surface, which would allow for greater removal efficiency. Improving the pH level of the carbon surface can be achieved by impregnating with caustic materials such as NaOH or KOH, which makes only a slight increase in the cost of materials. Other materials, such as KI, KMnO₄, K₂CO₃ and Na₂CO₃, are also used as impregnates for gas desulfurization. It has been reported that the total removal capacity could be increased as much as about 40-60 times that of the unmodified carbons, by impregnating with Na₂CO₃ (Xiao, Wang, Wu, & Yuan, 2008). Carbons are impregnated with iodine, alkali and metal hydroxides, oxides or carbonates, or nitrogen groups using urea or melamine (Bandosz T. J., 2006). The adsorption mechanism for impregnated carbon is not the same as for unmodified carbon, as the chemical reaction with hydrogen sulfide is irreversible with impregnated carbon. Impregnation with caustic materials also increases the selectivity towards sulfur formation (Mikhalovsky & Zaitsev, 1997).

The limitation in the application of caustic impregnated activated carbon is that impregnation decreases the ignition temperature of the carbon and poses a hazard of self-ignition. Another limitation is that the activity of caustic carbons towards hydrogen sulfide oxidation is exhausted when the caustic is consumed and the carbon pores are blocked by sulfur and sodium or potassium salts. The oxidation of hydrogen sulfide to sulfur either in direct oxidation or via dissociation to HS⁻ and its oxidation releases significant heat, and the risk of bed self-ignition is always there. (Bandosz T. J., 2006)

2.7 Proposed Mechanisms

There are several mechanisms proposed for dry and wet streams.

For wet streams with no oxygen the following mechanism was proposed by Adib et al. (Adib, Bagreev, & Bandosz, 2000)

\[
\begin{align*}
H₂S \text{ (gas)} & \rightarrow H₂S \text{ (ads)} \\
H₂S \text{ (ads)} & \rightarrow H₂S \text{ (ads - liq)} \\
H₂S \text{ (ads - liq)} & \rightarrow HS⁻ \text{ (ads)} + H⁺ \\
2HS⁻ \text{ (ads)} + O⁺(ads) & \rightarrow 2S\text{(ads)} + H₂O
\end{align*}
\]
where \( H_2S \) (gas), \( H_2S \) (ads-liq) and \( H_2S \) (ads) are concentration of hydrogen sulfide in gas, liquid film and adsorbed phases respectively. In step 1, the hydrogen sulfide is adsorbed onto the carbon surface, step 2 is the dissolution of hydrogen sulfide into the water film, step 3 is the dissociation of the hydrogen sulfide into ions, and step 4 is the surface reaction with oxygen functional group.

For wet streams, with oxygen, a different mechanism is proposed by Le Leuch et al. (Le Leuch, Subrenat, & Le Cloirec, 2003)

\[
\begin{align*}
H_2S \ (\text{gas}) & \rightarrow H_2S \ (\text{ads}) \\
O_2 \ (\text{gas}) & \rightarrow O_2 \ (\text{ads}) \\
H_2S \ (\text{ads}) & \rightarrow H_2S \ (\text{ads} - \text{liq}) \\
O_2 \ (\text{ads}) & \rightarrow O_2 \ (\text{ads} - \text{liq}) \\
C^* + O_2 & \rightarrow 2C(O^*) \\
H_2S \ (\text{ads} - \text{liq}) + H_2O & \rightarrow HS^- + H_3O^+ \\
HS^- (\text{ads}) + 2C(O^*)(\text{ads}) & \rightarrow S_2 (\text{ads}) + OH^- \\
HS^- (\text{ads}) + 3C(O^*)(\text{ads}) & \rightarrow SO_2 \ (\text{ads}) + OH^- \ (\text{side reaction}) \\
SO_2(\text{ads}) + C(O^*)(\text{ads}) & \rightarrow SO_3 \ (\text{ads}) \\
H^+ + OH^- & \rightarrow H_2O \\
SO_3 + H_2O & \rightarrow 2H^+ + SO_4^{2-}
\end{align*}
\]

where \( C^* \) is the reduced active site.

Bandosz (Bandosz T. J., 2001) also proposed a mechanism in relation to the pH level of the carbon surface for wet streams with oxygen which results in elemental sulfur.
In the above equations, $C_f$ represents free active sites. For strong acidic pH hydrogen sulfide does not dissociate.

Yan et al. suggested the following mechanism for alkaline carbons resulting in elemental sulfur, sulfur dioxide and further oxidation to sulfuric acid (Yan, Liang, & Tay, 2002).

\[
\begin{align*}
H_2S + H_2O & \rightleftharpoons HS^- + H_3O^+ \\
C_f + 0.5 O_2 & \rightleftharpoons C(O)
\end{align*}
\]

(Medium strength) Acidic $\leftarrow$ pH $\rightarrow$ Strong Basic

\[
\begin{align*}
HS^-_{(ads)} + C(O) & \rightarrow C(S^*) + H_2O \\
C(S^*) + O_2 & \rightarrow SO_{2(ads)} + C_f \\
SO_{2(ads)} + 0.5 O_2 & \rightarrow SO_{3(ads)} \\
SO_{3(ads)} + H_2O_{(ads)} & \rightarrow H_2SO_{4(ads)} \\
H_2SO_4 + H_2S & \rightarrow S_x + x H_2O \\
2 HS^-_{(ads)} + C(O) & \rightarrow C(SSH) + H_2O \\
C(SSH) + 2HS^- & \rightarrow C(S_3SH) + H_2O \\
C(S_n) & \downarrow
\end{align*}
\]

Carbonate species can also dissociate hydrogen sulfide to $HS^-$ ions, due to the alkaline nature of the carbonate by the mechanism below (Chen, et al., 2010).

\[
\begin{align*}
Na_2CO_3 + H_2O & \rightleftharpoons Na^+ + HCO_3^- + OH^- \\
H_2S + CO_{3^2} & \rightleftharpoons HS^- + H_2CO_3
\end{align*}
\]

Below is a diagram of the proposed adsorption mechanism by Chiang et al. (Chiang, Tsai, Chang, & Hsu, 2002) for sulfur autocatalytic reaction.
In steps 1 and 2, the hydrogen sulfide particles enter the graphite pore and get trapped. In Step 3 and 4, hydrogen sulfide particles are adsorbed and thiols are formed. In step 5 and 6, bonds are formed to make multi-sulfides and finally sulfur ring (S₈).

Chemisorption can also occur on hydroxide salts, via the below mechanism (Bagreev & Bandosz, 2002)

\[
\text{NaOH} + \text{H}_2\text{S} \rightleftharpoons \text{NaHS} + \text{H}_2\text{O}
\]

\[
2\text{NaOH} + \text{H}_2\text{S} \rightleftharpoons \text{Na}_2\text{S} + \text{H}_2\text{O}
\]

NaHS and Na₂S can be further oxidized, if the presence of water and oxygen, to form alkali groups which can under catalytic oxidation with hydrogen sulfide to form elemental sulfur (Bagreev & Bandosz, 2005) (Bagreev & Bandosz, 2002) (Bashkova, Armstrong, & Schwartz, 2009) (Cui, Turn, & Reese, 2009).

\[
\text{NaHS} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{S} + \text{NaOH}
\]

\[
\text{Na}_2\text{S} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{S} + 2\text{NaOH}
\]
The alkali hydroxide can then react with carbon dioxide to form carbonates (which can then catalyze the dissociation of hydrogen sulfide by alkaline nature), or react with hydrogen sulfide to form sulfides (Bagreev & Bandosz, 2005).

\[ 2\text{NaOH} + \text{CO}_2 \rightleftharpoons \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \]

\[ 2\text{NaOH} + \text{H}_2\text{S} + 2\text{O}_2 \rightleftharpoons \text{Na}_2\text{SO}_4 + 2\ \text{H}_2\text{O} \]

The following table compiled by Dalai et al. (Dalai, Cundall, & De, 2008) compares the kinetic data for a variety of activated carbon sources.

<table>
<thead>
<tr>
<th>Investigators</th>
<th>Catalyst</th>
<th>Reaction order with respect to O₂</th>
<th>Reaction order with respect to H₂S</th>
<th>Activation Energy, kJ/kmol (temperature range, °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Puri et al. (1971)</td>
<td>Activated charcoal</td>
<td>0.1</td>
<td>-</td>
<td>25.6 (120-240)</td>
</tr>
<tr>
<td>Sreeramamurthy and Menon (1975)</td>
<td>Activated carbon</td>
<td>0.5</td>
<td>1.0</td>
<td>6.7-29.3 (70-100)</td>
</tr>
<tr>
<td>Carioso and Walker (1975)</td>
<td>Activated carbon</td>
<td>0</td>
<td>1.0</td>
<td>20.1 (100-160) (measured), 40.2 (calculated)</td>
</tr>
<tr>
<td>Steijns and Mars (1974)</td>
<td>Carbon molecular sieve</td>
<td>0.5, O₂ &gt; 0.15%</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.75, O₂&lt;0.15%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Steijns and Mars (1974)</td>
<td>Activated carbon</td>
<td>0.2</td>
<td>0.24 ± 0.1</td>
<td>37 ± 4 (170-190)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>0.6 ± 0.06</td>
<td>Oxidation</td>
</tr>
<tr>
<td>Coskun and Tollefson (1980)</td>
<td>Activated carbon</td>
<td>-</td>
<td>0.5</td>
<td>23.4-48.9 (24-152)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>21.2-28.5 (70-188)</td>
</tr>
<tr>
<td>Klein and Henning (1984)</td>
<td>Activated carbon</td>
<td>0.5, H₂S:O₂&gt;1</td>
<td>0.8</td>
<td>28-40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0, H₂S:O₂ &lt;1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Authors</td>
<td>Treatment</td>
<td>Activity</td>
<td>Selectivity</td>
<td>Hygroscopic Capacity</td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------------------------</td>
<td>----------</td>
<td>-------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Ghosh and Tollefson (1986)</td>
<td>Activated carbon</td>
<td>-</td>
<td>-</td>
<td>23.63</td>
</tr>
<tr>
<td>Dalai et al. (1993)</td>
<td>Activated carbon</td>
<td>1.0</td>
<td>1.0</td>
<td>2.6 (T&gt;130)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.9 (T&lt;130)</td>
</tr>
<tr>
<td>Dalai and Tollefson (1998)</td>
<td>Activated carbon</td>
<td>-</td>
<td>-</td>
<td>34.2 (125-200)</td>
</tr>
<tr>
<td>Wang et al. (2006)</td>
<td>Na₂CO₃ impregnated activated carbon</td>
<td>-</td>
<td>-</td>
<td>29.9 (30-80)</td>
</tr>
<tr>
<td>Dalai et al. (2008)</td>
<td>NH₄I impregnated activated carbon</td>
<td>-</td>
<td>-</td>
<td>40 (125-175)</td>
</tr>
</tbody>
</table>
Chapter 3
Adsorption Models

3 Adsorption Models

3.1 Packed-Bed Dynamics and Breakthrough Curves

It is the overall dynamics of a packed-bed system that governs the design and efficiency of the given process. In an ideal plug flow system with no resistance to mass transfer, the outlet concentration response would replicate the input with a time delay corresponding to the hold-up in the column. However, in a real system that does not follow ideal plug flow, the outlet response is dispersed as a result of the combined effects of axial dispersion and mass transfer resistance. Therefore, measurement of the time delay provides information on adsorption equilibrium, while measurement of the dispersion of the response provides information on the adsorption kinetics and the extent of axial mixing. In order to extract this information, the experimental response curve must be matched to the correct theoretical model for the system (Ruthven, 1984). It is also possible to predict the outlet response curve from basic kinetic and equilibrium data, however, this data would have to be obtained through extensive experimentation. Furthermore, as there are simultaneous chemical and physical adsorption mechanisms occurring in this case, it is impossible to distinguish between each mechanism and equilibrium adsorption data cannot be found through the usual experimental techniques such as constant volume method, dynamic method, gravimetric method, or chromatographic method (Yang, 1987). With information on the behaviour of the packed-bed adsorption, the engineer is able to design the column and optimize the separation efficiency.

To study the dynamics of a fixed-bed adsorption column, the outlet response of an initially adsorbate free column is analyzed. Two methods are commonly used, the first is a step change in the adsorbate inlet concentration, the second, an injection of a small pulse of adsorbate at the inlet (pulse input). The outlet response curve to a step input is called a breakthrough curve, while the response to a pulse input is called a chromatographic response. In this study, breakthrough curves are used to study the dynamics of the system since the adsorption is irreversible and no chromatographic response can be obtained. Adsorbate concentration in the flow at any given point in the bed is a function of time, resulting from the concentration front moving down the
bed. The shape and width of the curve is significantly important in the design of adsorbers. A sharp concentration front is desirable for efficient separation, as a more dispersed front indicates both mass and heat dispersions in the axial direction, and resistances to heat/mass transfer within the particle.

The breakthrough curve for a gas containing a single adsorbate is obtained by the solution of the mass balance equations for both the bed and sorbent particle, along with the equilibrium isotherm. Analytical solutions are available for a number of simple and limited cases involving a single adsorbate.

All models for an adsorption bed must include the following:

i) The adsorption isotherm relationship

ii) Mass balance on the inter-pellet gas phase

iii) Mass balance on each pellet

Often, fixed bed absorbers and heterogeneous chemical reactors are modeled similarly. In reactor modeling, the local reaction rate is finite and the reaction is assumed irreversible for the sake of mathematical simplicity. Under circumstances when the reaction is reversible and the reaction rate is much higher than transport rates in an adsorption process, the models for reactors and adsorbers are identical. As seen from experimental results, when hydrogen sulphide is adsorbed onto the activated carbon surface, sulfur is detected on the carbon surface afterwards. As such, a chemical reaction proceeds during the adsorption and the model must account for both physisorption and chemisorption. As there is no experimental evidence indicating chemical reaction dominance (reaction rate much higher than transport rates), the model will include both adsorption mechanisms. Most analytical solutions available in literature (Yang, 1987) (Rodrigues, 1981) (Vermeulen, Klein, & Hiester, 1973) account for only physisorption and no chemical reaction; however, a few simplified solutions will be explored later on.

### 3.2 Factors to Consider when Choosing the Correct Theoretical Model

Each theoretical model starts with differential mass balance/continuity equations. Deciding on the correct model for the process studied depends on the following factors:

i) The assumption of equilibrium or non-equilibrium behaviour
ii) Inclusion or exclusion of axial dispersion effects

iii) The type of rate law used (when non-equilibrium exists)

iv) The type of adsorption isotherm characterizing the system

v) Inclusion or exclusion of chemisorption (chemical reaction), and the reaction rate expression

From analyzing the experimental breakthrough curve, shape of the breakthrough curve, and using trial and error, the appropriate model can be found for the process under study. With the use of experimental breakthrough curves, kinetic parameters accounting for axial dispersion, external and internal mass-transfer resistances, as well as the effect of adsorbate deposition on the inner-face of the catalyst can be found (catalyst degradation). These constants are needed for a full solution of the model which then can be used for simulation studies, scale-up, and process design. The model yields a complete set of flow velocity, concentration as a function of time and location in the bed. From this data, all important results for the separation process such as product purity, product recovery and productivity can be calculated.

When equilibrium theory is followed it is assumed that instant equilibrium is reached in the bed between the bulk flow and the adsorbed phase (Yang, 1987). This assumption is valid for fast adsorption processes that are not hindered by mass transfer resistances. A common assumption used to solve fixed-bed adsorption problems is that the solution phase and the adsorbent phase throughout the bed are in equilibrium. This condition is achieved if the uptake of adsorbate is fast or if the residence time of the solution in the bed is long. If the equilibrium is maintained, one has

\[ q = f(c_b) \]

for simple component systems, where \( q \) is the mass adsorbed per unit mass of carbon, and \( c_b \) is bed concentration in mass adsorbate per unit volume challenge gas.

The shape of the breakthrough curve is heavily governed by the nature and type of equilibrium isotherm followed (Ruthven, 1984) in the case where chemical reaction does not occur.

The equilibrium isotherm can be classified into the following types

- A (linear isotherm): \( K_d = 1 \) and \( d^2q^*/dC^2 = 0 \)
- B (favourable isotherm): $K_d > 1$ and $d^2q^*/dC^2 < 0$
- C (unfavourable isotherm): $K_d < 1$ and $d^2q^*/dC^2 > 0$

For non-equilibrium models, the effect of mass transfer resistance is included in the model with the inclusion of constants such as overall film mass transfer coefficient ($k$), molecular diffusivity ($D_m$), surface diffusivity ($D_s$) and effective diffusivity ($D_e$). These values are readily found through correlations in literature.

Film mass transfer coefficient can be found using the following correlations. First the molecular diffusivity can be found using the Fuller-Schlettler-Gridding method (Equation 3.1) used for a binary gas mixture; in this case hydrogen sulphide and nitrogen gas.

$$D_m = \frac{0.00143T^{1.75}}{PM_{AB}^{1/2} \left[ \left( \sum V_A^{1/3} \right) + \left( \sum V_B^{1/3} \right)^2 \right]} \quad (3.1)$$

Where $P$ is pressure, $T$ is temperature, $M_{AB}$ is molecular weight of gas mixture, and $V$ is the special diffusion parameters. Once the Schmidt number (Equation 3.2) and Reynolds number (Equation 3.3) are calculated, the Sherwood number can be found using the Wakao-Funazkri correlation (Equation 3.5). The Sherwood number (Equation 3.4) can then be used to find the film mass transfer coefficient (Equation 3.5),

$$Sc = \frac{\mu_f}{\rho_f D_m} \quad (3.2)$$

$$Re_p = \frac{d_p U \rho_f}{\mu_f} \quad (3.3)$$

$$Sh_p = 2 + 1.1 Sc^{1/3} Re_p^{0.6} \quad (3.4)$$

$$Sh_p = \frac{k_f d_p}{D_m} \quad (3.5)$$

where $\mu_f$ is the fluid viscosity, $\rho_f$ is the fluid density, $d_p$ is the particle diameter, and $U$ is the fluid superficial velocity. The governing equations for a model which includes mass transfer resistance are,
where $C$ is the fluid concentration, $C^p$ is the particle concentration, $D_Z$ is the axial dispersion coefficient, $u$ is the interstitial velocity, $z$ is the distance along the bed length, $t$ is time, $\varepsilon$ is the interpellet void fraction, $k$ is the average film mass transfer coefficient, $a$ is the exterior surface area of the particles per volume of bed, $C^p_R$ is the concentration at the particle surface, $R$ is the radius of the particle, $q$ is the sorbate concentration in the particle, $D_e$ is the effective diffusivity, and $r$ is the radial distance in the particle.

Axial dispersion results from significant wall effects if the ratio of the bed-to-particle diameter is not sufficiently large. The ratio of bed diameter to particle diameter should be in the magnitude of 20 or greater. There are two main mechanisms which contribute to axial dispersion: molecular diffusion and turbulent mixing arising from the flow around the adsorbent particles. Axial mixing is undesirable, as it reduces the separation efficiency of the process. Therefore, it is a major design objective to minimize such mixing. Axial dispersion can be accounted for in the model by using a lumped coefficient ($D_L$) which accounts for all mechanisms which contribute to axial mixing. Studies done by Wakao (Wakao & Funazkri, 1978) have shown that correlations used to predict $D_L$ for non-porous adsorbents are not valid for porous adsorbents. If the adsorption or reaction within the particle is strong and rapid, the concentration profile within the particle becomes asymmetric. The asymmetric concentration profile increases axial dispersion due to the allowance of direct transport through the particle (intraparticle diffusion). The effect of intraparticle diffusion on the diffusion coefficient depends on the effective intraparticle diffusivity and the magnitude of the concentration gradient through the particle. This effect is only significant at lower Reynolds number, as at high Reynolds number there is sufficient turbulent mixing to ensure uniform boundary concentration around particles. Furthermore, the effect is more pronounced for adsorption that occurs outside of the particle, such as during the initial stages of the breakthrough curve. Wakao has given the following expression to determine $D_L$ (Equation 3.8).
The practical significance of the above correction to the correlation for non-porous adsorbents is that with strongly adsorbed species under laminar flow conditions, axial dispersion may be important even when it would be insignificant for nonporous particles. There are also more detailed models that include other dispersion effects such as radial dispersion; however, the complexity is not necessary to accurately predict the response curve. In the instance that both ideal plug flow is followed and the dispersion coefficient is significantly low, the dispersion term (first term in equation 3.6) can be neglected in porous particle adsorption.

3.3 Incorporating Proposed Mechanisms of Hydrogen Sulfide Adsorption into an Adsorber Model

The mechanism by which hydrogen sulphide is adsorbed onto the carbon surface is not yet fully understood. There are several mechanisms that have been proposed, where the presence of oxygen makes a difference. Water also plays a significant role in the adsorption of hydrogen sulfide onto the carbon by dissociating H₂S into ions and slowing down the deactivation process by promoting deposition and adsorption of sulfur on different active sites. From the proposed mechanisms in section 2.7, the following factors must be considered for the adsorber model:

- Physisorption of hydrogen sulfide via Van der Waal forces, following a Langmuir isotherm as commonly used in other sources (Dalai, Cundall, & De, 2008)

- Mass transport phenomena due to the presence of water film in relation to adsorption. This can be included into the model using a film transfer coefficients.

- If non-equilibrium or equilibrium conditions exist. In literature (Bandosz T. J., 2006), instantaneous reactions on the carbon surface and in the water film are assumed.

- Chemisorption and the reaction kinetics order (first order, second order, etc.) with respect of hydrogen sulfide and oxygen.

- Catalyst degradation as pores are being filled and active sites are blocked, and active groups (oxidizing group) are consumed.
3.4 Models Studied

3.4.1 Introduction

The sections to follow explore six different adsorption models which were studied and fitted with experimental data for analysis. Each model is different from the other in terms of the type of adsorption isotherm, inclusion or exclusion of chemical reaction, significant or negligible mass transfer resistance, chemical reaction kinetics, and the type of rate law used if non-equilibrium is assumed. The governing equations and solution for each model are presented and explained, however, the full solutions have not been included in this thesis. The full solutions are referenced within each section and can be found in the original author’s publication.

One example of curve fitting is displayed for each model, which shows the full experimental breakthrough curve compared to the model prediction. By comparing the full curve, a more accurate assessment can be made, as the initial part of the curve before the second inflection point, can be easily fitted by numerous models. The models are each assessed on how well they fit the data using linear regression, and if the governing equations include all the mechanisms that occur in hydrogen adsorption on activated biochar. The same analysis of all models was done for every experimental run performed by Andrew White.

3.4.2 Adam and Bohart Model

3.4.2.1 Theory

Adam and Bohart proposed a model for one component adsorption that has been widely used to describe adsorption dynamics when chemical reaction takes place. It was found that this model can be used to describe the initial part of the breakthrough curve for many one component adsorption systems with chemical reaction. The model incorporates an irreversible adsorption isotherm, which indicates that any solute adsorbed onto the carbon surface cannot desorb. However, no real isotherm in the world is completely irreversible, but many are sharp enough to justify modeling systems with the irreversible assumption. (Bohart & Adams, 1920)

Mass balance (continuity) equation for the fixed bed adsorption column is below:

\[
\frac{\partial C}{\partial t} + v \frac{\partial C}{\partial x} + \frac{(1 - \varepsilon)}{\varepsilon} \frac{\partial q}{\partial t} = 0 \quad (3.9)
\]
where $C$ is the adsorbate concentration in the gas stream (g adsorbate/L gas), $t$ is time (s), $v$ is superficial velocity of the gas stream (dm/s), $x$ is distance from the column inlet, $\varepsilon$ is bed porosity (dimensionless), and $q$ is the adsorbate concentration in the adsorbent (g adsorbate/L adsorbent). Kinetics of adsorption are described using the quasichemical rate law below:

$$\frac{\partial q}{\partial t} = kC(q_e - q) \quad (3.10)$$

where $q_e$ is the constant value of $q$ that corresponds to the equilibrium condition at the gas/adsorbent interface (g adsorbate/L carbon), and $k$ is a constant. The rate of adsorption (quasichemical rate law) is proportional to the concentration of the adsorbate in the gas, and to the fraction of the capacity of the adsorbent which still remains at a moment in time. The model uses the rectangular, irreversible isotherm normally used to describe reaction systems.

$$q_e = \begin{cases} 
0, & \text{if } C = 0 \\
q_s, & \text{if } C > 0
\end{cases} \quad (3.11)$$

For negligible axial dispersion, the differential mass balance was solved by Cooney (Cooney, 1999) and the solution below was obtained:

$$\frac{C}{C_0} = \frac{\exp(\tau)}{\exp(\tau) + \exp(z) + 1} \quad (3.12)$$

where

$$\tau = kC_0\left(t - \frac{x}{u}\right) \quad (3.13)$$

and

$$z = \frac{kq_sx}{u\left(1 - \varepsilon\right)} \quad (3.14)$$

where $q_s$ is the adsorptive capacity of the adsorbent (g/L).
3.4.2.2 Application

By re-arranging the above equation 3.12, the linear form below is obtained.

\[ \ln\left(\frac{C_0 - C}{C}\right) = -kC_0\left(t - \frac{x}{u}\right) + \ln\left\{\exp\left[\frac{kq_xxe}{u(1 - \varepsilon)}\right] + 1\right\} \quad (3.15) \]

By plotting \(\ln(C_0-C/C)\) versus \((t - x/u)\), a linear relationship is expected if the Adam and Bohart model fits the experimental data. From Figure 3.4.1 below, it can be seen that the relationship is not linear, and the \(R^2\) value is 0.8446.

**Figure 3.4.1 – Adam and Bohart Model Linear Regression**

From comparison of the Adam and Bohart model prediction to the experimental data, discrepancies between the inflection point and the overall shape of the curve can be seen. The Adam and Bohart model is unable to follow the non-symmetrical shape of the experimental data,
which concludes that a lumped quasichemical rate expression is insufficient in describing the mechanisms of hydrogen sulfide adsorption on activated carbon.

**Experimental vs. Model**

![Experimental vs. Model](image)

**Figure 3.4.2 – Adam and Bohart Model vs. Experimental Data**

### 3.4.3 Thomas Model

#### 3.4.3.1 Theory

Thomas (Thomas, 1944) developed a model that uses Langmuir isotherm for equilibrium, and 2\textsuperscript{nd} order reversible reaction kinetics based on ion exchange theory.

The continuity equation of the column is written as,

\[
\nu \frac{\partial c}{\partial x} + \frac{\partial c}{\partial t} + \frac{\rho}{\varepsilon} \frac{\partial q}{\partial t} = 0 \quad \text{(3.16)}
\]

where \( \nu \) is the linear rate of flow of gas (dm/s), \( c \) is the adsorbate concentration in the gas stream (g adsorbate/L gas), \( q \) is the adsorbate concentration in the carbon (g adsorbate/g carbon), \( x \) is the distance from the bed inlet (dm), \( t \) is time (s), \( \rho \) is bulk density of the carbon (g/dm\(^3\)), and \( \varepsilon \) is porosity of the bed (dimensionless).
The expression for adsorption kinetics is described as,

\[
\frac{\partial q}{\partial t} = k_1(q_0 - q)c - k_2q(c_0 - c) \quad (3.17)
\]

where \(k_1\) and \(k_2\) are velocity constants (s\(^{-1}\)), \(q_0\) is the initial ion exchange capacity of the carbon (g adsorbate/g carbon), and \(c_0\) is the inlet concentration of adsorbate in the gas stream (g adsorbate/L). The above expression describes 2\(^{nd}\) order reversible reaction kinetics, it assumes a constant separation factor which can be applicable to both favorable and unfavorable adsorption conditions. Adsorption is generally not limited by chemical reaction kinetics but controlled by interphase mass transfer. Therefore, the model proposed by Thomas is suitable for adsorption processes where external and internal diffusion limitations are absent. (Srivastava, Prasad, Mishra, Mall, & Swamy, 2008)

The initial and boundary conditions for the system are stated below.

- At \(t = 0, x \geq 0\), \(q = 0\)
- At \(x = 0, t \geq 0\), \(c = c_0\)

By assuming plug flow, negligible axial dispersion, the above continuity equation was solved by Thomas to obtain the solution below for long bed lengths,

\[
\frac{C}{C_0} = \frac{1}{1 + \exp [k_T(q_0m_c - C_0V_{eff})/Q]} \quad (3.18)
\]

where \(k_T\) is the Thomas rate constant (dm\(^3\)/(s*g)), \(q_0\) is the adorptive capacity of the carbon (g/g), \(m_c\) is the mass of carbon in the column (g), \(V_{eff}\) is the throughput volume (L), and \(Q\) is the volumetric flow rate (dm\(^3\)/s).

### 3.4.3.2 Application

The above equation can be linearized to give,

\[
\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_Tq_0m_c}{Q} - k_TC_0t \quad (3.19)
\]
where $V_{eff}/Q = t$. A plot of $\ln(C_0/C - 1)$ vs. $t$ of the experimental data for activated biochar run 03122010, should give a linear relationship if the above model is correct. Below in Figure 3.4.3, is the linear regression of the experimental data showing a $R^2$ value of 0.8446. However, it is visible from the shape of the curve that the relationship is not linear.

**Thomas Model - Linear Regression**

![Graph showing linear regression with equation $y = -0.035x + 5.1891$ and $R^2 = 0.8446$.](image)

Figure 3.4.3 - Thomas Model Linear Regression

Comparing the model predicted breakthrough curve with the experimental data in Figure 3.4.4 below, it can be observed that the model does not have the same inflection points as the experimental data. Furthermore, the shape of the model curve is symmetrical, whereas, the experimental curve is not. This is an indication that the model does not correctly represent the physical and chemical adsorption mechanisms of hydrogen sulfide on activated biochar. It was found in literature (Srivastava, Prasad, Mishra, Mall, & Swamy, 2008) that application of this model can lead to some error in sorption processes that follow first-order reaction kinetics. Therefore, the Thomas model was not considered an ideal fit for hydrogen sulfide adsorption on activated biochar.
3.4.4 Yoon and Nelson Model

3.4.4.1 Theory

Theoretical model developed by Yoon and Nelson (Yoon & Nelson, 1984) is based on gas adsorption kinetics and the assumption that the rate of decrease in the probability of adsorption for each molecule is proportional to the probability of sorbate adsorption and the probability of sorbate breakthrough on the sorbent. It follows that,

\[- \frac{dQ}{dt} \propto QP \]  \hspace{1cm} (3.20)

where Q (%) is the probability for adsorption, P (%) is the probability for breakthrough, and t (s) is time. Experimental evidence also shows that the rate of decrease in the probability of adsorption is directly proportional to the gas (contaminant concentration) C (g adsorbate/L), and
the volumetric flow rate \( U \) (L/s), and inversely proportional to the weight of the carbon \( W_c \) (g adsorbent) (Yoon & Nelson, 1984). Therefore,

\[
- \frac{dQ}{dt} \propto \frac{CU}{W_c} QP \quad (3.21)
\]

by introducing a dimensionless constant of proportionality, \( k \), we have

\[
- \frac{dQ}{dt} = \frac{kCU}{W_c} QP \quad (3.22)
\]

or,

\[
- \frac{dQ}{dt} = k_{YN} QP \quad (3.23)
\]

where \( k_{YN} = \frac{CU}{W_c} \).

Solving the above differential using the boundary condition where at 50% breakthrough, \( t = t_{0.5}, Q = 1/2 \) and \( P = \frac{1}{2} \). The following solution is obtained,

\[
\ln \left( \frac{C}{C_0 - C} \right) = k_{YN} t - t_{0.5} k_{YN} \quad (3.24)
\]

where \( C_0 \) is the inlet concentration (g adsorbate/L gas).

### 3.4.4.2 Application

By plotting experimental values of \( \ln(C/C_0 - C) \) as a function of \( t \), the expected curve should be linear if the model fits the data. Below in Figure 3.4.5, it can be seen that the relationship is not linear, and the \( R^2 \) value is 0.8446.
In Figure 3.4.6 below, the model predicted breakthrough curve is compared to the experimental data, it can be observed that the model does not have the same inflection points as the experimental data. Furthermore, the shape of the model curve is symmetrical, whereas, the experimental curve is not. From the comparison of the model to the experimental data, it can be concluded that a simple model based on probability cannot accurately model the physical and chemical adsorption mechanisms of hydrogen sulfide on activated biochar. Therefore, the Yoon and Nelson model was not considered an ideal fit for hydrogen sulfide adsorption on activated biochar.
3.4.5 Clark Model

3.4.5.1 Theory

Model developed by Clark is based on the use of mass transfer concept in combination with the Freundlich isotherm (Clark, 1987). Gas phase mass balance within a differential element in the fixed bed adsorber can be described in the equation below:

\[
J = \frac{v_s A C - v_s A (C - \Delta C)}{A \Delta z}
\]  

(3.25)

where \( J \) is the mass transfer rate per unit reactor volume (g adsorbate/(s*L)), \( v_s \) is the superficial velocity of gas per unit of cross-sectional area (dm/(s*dm²)), \( A \) is the column cross sectional area (dm²), and \( C \) is the influent adsorbate concentration into the differential element volume (g/L), and \( z \) is the reactor height (dm). Simplifying and taking the limit below,
\[ \lim_{{\Delta z \to 0}} \frac{\Delta C}{\Delta z} = \frac{dC}{dz} \quad (3.26) \]

then equation 3.25 can be simplified to the equation below.

\[ J = v_s \frac{dC}{dz} \quad (3.27) \]

The following mass transfer coefficient concept is used,

\[ k_T (C - C_e) = v_s \frac{dC}{dz} \quad (3.28) \]

or rearranged to,

\[ \frac{dC}{C - C_e} = \frac{k_T dZ}{v_s} \quad (3.29) \]

where \( k_T \) is the mass transfer coefficient in \((s^{-1})\), and \( C_e \) is the equilibrium value of adsorbate at the gas/carbon interface \((g \text{ adsorbate/dm}^3 \text{ carbon})\). With the assumption that all gas is removed at the end of the column, the ideal mass balance over the entire column is:

\[ v_s C = L_a q \quad (3.30) \]

or rearranged to,

\[ \frac{C}{q} = \frac{L_a}{v_s} \quad (3.31) \]

where \( L_a \) is the mass velocity of adsorbent to keep the mass transfer zone stationary \((g \text{ carbon/s*dm}^{-2})\), and \( q \) is the concentration of adsorbate per unit weight of adsorbent \((g \text{ adsorbate/g carbon})\). Using the Freundlich isotherm between the adsorbent and gas yields

\[ X = K(C_e)^{\frac{1}{n}} \quad (3.32) \]

or,

\[ C_e = (1/K)^n X^n \quad (3.33) \]
where $K$ is the equilibrium constant and $1/n$ is the slope of the isotherm. Substituting equations 3.31 and 3.33 into 3.29 yields equation 3.34 below.

$$\frac{dC}{C - \left(\frac{1}{K} \left(\frac{v_s}{L_a}\right)^n\right)C^n} = \left(\frac{k_T}{v_s}\right)dZ \quad (3.34)$$

Using the boundary condition below,

- At $t = t_b$ (breakthrough time), $C = C_b$ (concentration at breakthrough time)

equation 3.34 was solved by Clark and the solution below was found where $n \neq 1$,

$$\frac{C}{C_0} = \left(\frac{1}{1 + Ae^{-rt}}\right)^{1/(n-1)} \quad (3.35)$$

where,

$$A = \left(\frac{C_0^{n-1}}{C_b^{n-1}} - 1\right)e^{rt_b} \quad (3.36)$$

$$r = R(n - 1) = \frac{k_T}{v_s}V_m(n - 1) \quad (3.37)$$

where $V_m$ is the migration velocity of the concentration front in the bed (dm/s) and can be determined from the relationship below,

$$V = \frac{uC_0}{N_0 + C_0} \quad (3.38)$$

where $u$ is the gas flow rate (L/s) and $N_0$ is the adsorptive capacity of the carbon (g adsorbate/L carbon).

### 3.4.5.2 Application

Equation 3.35 can be rearranged into the following linear form.

$$\ln\left[\frac{C_0}{C}^{n-1} - 1\right] = -rt + lnA \quad (3.39)$$
By plotting the experimental values of $\ln[(C_0/C)^{n-1} - 1]$ versus $t$, the plot should be linear if the above model fits the experimental data. From Figure 3.4.7, it can be seen that after optimizing the value of $n$ to approach 1, the linear regression of the experimental data is almost linear, with a $R^2$ value of 0.9585.

![Linear Regression](image)

**Figure 3.4.7 – Clark Model Linear Regression**

From comparison of the Clark model prediction to the experimental data, a fairly good agreement is seen between the inflection points, and the model is able to mimic the non-symmetrical shape of the experimental data. The Clark model would be very close to an ideal fit, however, $n \neq 1$ according to solution 3.35. Therefore, the Clark model cannot be used to model the adsorption of hydrogen sulfide on activated biochar. However, from this model, a few points can be concluded. It is expected that the correct model is first order in either physical adsorption or chemical adsorption (as only one mechanism is accounted for in this model), and a limiting factor must be included, in this model it is the mass transfer concept.
3.4.6 Wolborska Model

Wolborska found that the breakthrough had two regions in which the migration rate of the concentration front is described in different ways (Wolborska, 1989).

1. A low concentration region in the range from $10^{-5}$ to $5\times10^{-2}$ of the normalized outlet concentration ($C_{\text{outlet}}/C_{\text{inlet}}$)

2. A high concentration region containing the other range of the curve

The model developed by Wolborska is solely for the low concentration region of the breakthrough curve and based on the following observations from Dubinin et al (Dubinin, Nikolaev, Poljakov, & Petrova, Investigation of adsorption dynamics in a broad range of breakthrough concentrations. Part 2., 1972) (Dubinin, Nikolaev, Poljakov, & Pirozhkov, 1980).

- Formation of the low concentration region takes place in the initial stage of the process
• The initial concentration distribution is translocated along the column at a constant velocity

• The width of the breakthrough curve in the range of low concentration is constant

• The low concentration area is characterized by constant kinetic coefficients

• The process rate is controlled by the external mass transfer resistance (Wolborska, 1989)

Below is the continuity equation on the column:

\[
\frac{\delta c}{\delta t} + u \frac{\delta c}{\delta h} + \frac{\delta q}{\delta t} = D \frac{\delta^2 c}{\delta h^2} \quad (3.40)
\]

where \(c\) is the adsorbate concentration in the gas phase (g adsorbate/L gas), \(t\) is time (s), \(u\) is the flow rate (L/s), \(q\) is the adsorbate concentration in the solid phase (g adsorbate/g adsorbent), \(D\) is axial diffusion coefficient, and \(h\) is the distance from the column inlet (dm).

The initial condition at \(t = 0\) is \(c(z,0) = 0, q(z,0) = 0\).

The boundary conditions are at \(z = 0\), \(c(0,t) = c_0\) (inlet concentration), and at \(z = \infty\), \(c(\infty,t) = 0\).

Introducing new variables time \(\tau = t\) and \(z = h – wt\), where \(w = \text{constant}\). Then equation 3.40 becomes:

\[
(u – w) \frac{dc}{dx} – w \frac{dq}{dx} = D \frac{d^2c}{dx^2} \quad (3.41)
\]

and the initial and boundary conditions are \(c(x,0) = 0, q(x,0) = 0, c(0,\tau) = c_0, \text{and } c(\infty,\tau) = 0\).

Since the process is assumed to be external diffusion controlled, a constant kinetic coefficient is used in the kinetic equation derived below,

\[
\frac{\delta q}{\delta t} = \beta(c – c_i) \quad (3.42)
\]
where $c_i$ is the concentration at the gas/adsorbent interface. The diffusion into the carbon particles are fast enough to assume the adsorbate concentration at the interface satisfies the condition, $c_i << c$. Then,

$$-w \frac{dq}{dx} = \beta_0 c \quad (3.43)$$

where $\beta_0 = \beta$ when $t \to 0$.

Inserting expression 3.43 into equation 3.41, the following differential equation is obtained.

$$\frac{d^2 c}{dx^2} - \frac{(u - w) dc}{D} - \frac{\beta_0 c}{D} = 0 \quad (3.44)$$

Wolborska solved the above differential and found the following solution in the original variables,

$$\ln \frac{c}{c_0} = \beta_a c_0^t - \frac{\beta_a}{u} h \quad (3.45)$$

where for process without axial diffusion

$$\beta_a = \beta_0$$

and for column dynamics with axial dispersion.

$$\beta_a = \frac{u^2}{2D} \left( \sqrt{1 + \frac{4\beta_0 D}{u^2}} - 1 \right) \quad (3.46)$$

3.4.6.1 Application

By plotting $\ln(c/c_0)$ versus $t$ of the experimental data, the resulting curve would be linear should the Wolborska model solution fit the data. From Figure 3.4.7, it can be seen that the relationship is not linear, and the $R^2$ value is 0.6265.
Figure 3.4.9 – Wolborska Model Linear Regression

From comparison of the Wolborska model prediction to the experimental data in Figure 3.4.10, it can be seen that the model is a poor fit to the data. In particular, the model struggles to model the higher concentration range of the breakthrough curve. Which is reasonable, as the model is developed based on the low concentration range. Therefore, the Wolborska model is not a valid model to represent the adsorption of hydrogen sulfide on activated biochar.
Zhang and Cheng developed a model based on the catalytic hydrolysis reaction of cyanogen chloride in a fixed carbon bed adsorber, which in this paper, will be explored in the application of hydrogen sulfide catalytic oxidation. It was assumed that physical adsorption and catalytic self-deactivation reaction occurred simultaneously as impregnated carbon removed cyanogen chloride. The reaction products cover parts of all of the active sites resulting in catalyst deactivation. (Zhang & Cheng, 2000) A first-order deactivation reaction is assumed and the deactivation rate equation is:

\[
\frac{\partial \phi}{\partial t} = K_d \phi \quad (3.47)
\]

where \( t \) is time (s), \( \phi \) is the deactivation function (dimensionless), and \( K_d \) (s\(^{-1}\)) is the deactivation rate constant. Given the initial condition, when \( t = 0 \), then \( \phi = 1 \), and taking the derivative of 3.47, equation 3.48 is obtained for the deactivation function. The solution below is true for

---

**Figure 3.4.10 – Wolborska Model vs. Experimental Data**
separable deactivation kinetics resulting from contact with a catalyst poison at a constant concentration (inlet concentration) and no spatial variation (Fogler, 2005).

\[
\phi = e^{-K_d t} \quad (3.48)
\]

The chemical reaction also follows a first-order reaction and the rate equation is:

\[
R = KC\phi = KCe^{-K_d t} \quad (3.49)
\]

where \( R \) is the reaction rate (g/Ls), \( K \) is the reaction rate constant (s\(^{-1}\)), \( C \) is the adsorbate concentration in the gas stream (g/L). Assuming that the bed dynamics follow ideal plug flow with no axial dispersion, and isothermal conditions, then the superficial gas velocity is kept constant and the continuity equation of the fixed bed adsorber is as follows:

\[
\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + \frac{1 - \varepsilon}{\varepsilon \rho} \frac{\partial q}{\partial t} + R = 0 \quad (3.50)
\]

where \( u \) is superficial velocity (dm/s), \( x \) is the distance from the bed inlet (dm), \( \varepsilon \) is bed porosity (dimensionless), \( q \) is the adsorbate concentration in the carbon (g adsorbate/g carbon), and \( \rho \) is the bulk density of the carbon (g/dm\(^3\)).

The physical adsorption is characterized by a linear isotherm as at small concentrations, the Langmuir isotherm is linear (Zhang & Cheng, 2000).

\[
q = K_i C \quad (3.51)
\]

Then taking the derivative of equation 3.51 with respect to time, the following expression is obtained,

\[
\frac{\partial q}{\partial t} = K_i \frac{\partial C}{\partial t} \quad (3.52)
\]

where \( K_i \) is the adsorption constant in (L gas/g carbon).

The above partial differential equation 3.50 was solved by Zhang et al. (Zhang & Cheng, 2000) using the stream line method and the boundary conditions below.

- At \( x = 0, t > 0, C = C_0 \)
- At \( t = 0, x > 0, C = 0 \)
The following solution is given below (full solution also found in Appendix B).

\[
\ln \ln \frac{C_0}{C} = \ln \left[\frac{K}{1 + \frac{K_i \rho (1 - \varepsilon)}{\varepsilon}}\right] K_d t + \ln \left\{e^{\frac{K_d x}{u}} \left[1 + \frac{K_i \rho (1 - \varepsilon)}{\varepsilon}\right] - 1\right\} \quad (3.53)
\]

If the bed height \( x \) is constant, the breakthrough curve can be linearized and written as:

\[
\ln \ln \frac{C_0}{C} = a - K_d t \quad (3.54)
\]

where,

\[
a = \ln \frac{K}{\alpha K_d} + \ln \left(e^{\frac{K_d x L}{u}} - 1\right) \quad (3.55)
\]

\[
\alpha = 1 + \frac{K_i \rho (1 - \varepsilon)}{\varepsilon} \quad (3.56)
\]

where \( L \) is the length of the bed (dm).

3.4.7.1 Application

By plotting \( \ln \ln (C_0/C) \) versus \( t \), a linear relationship is expected should the Zhang and Cheng model fit the experimental data. From Figure 3.4.11 below, it can be seen that the data follows a fairly linear relationship, and the \( R^2 \) value is 0.9593.
Comparison of the model prediction to the experimental data also showed good agreement between the inflection points and the shape of the curve (non-symmetric). This indicates that the Zhang and Cheng model has the correct mechanisms included in the governing equations to represent the adsorption behavior of hydrogen sulfide on activated biochar. Therefore, the Zhang and Cheng model will be used to model the adsorption of hydrogen sulfide on activated biochar.
3.5 Summary

From the models studied above, the best data fit was obtained with the Clark model and the Zhang and Cheng model. However, for the Clark model the best fit was obtained for n value approached 1, and the limitation is that n ≠ 1. The Zhang and Cheng model also showed superior fit, with better R² values, in comparison to all other models for every experimental run (all data included in Appendix C). Therefore, of all the models studied, the Zhang and Cheng model best fits the data. Furthermore, the model incorporates mechanisms of hydrogen sulfide adsorption into the governing equation which is in agreement with experimental observations and literature (explored further in Chapter 4). The Zhang and Cheng model is able to fit the data properly as it incorporates two separate terms for chemical and physical uptake. Whereas, all other models explored had lumped both mechanisms into one term, or only accounted for physical adsorption. This indicates that adsorption of hydrogen sulfide by activated biochar follows both physisorption and chemisorption. Furthermore, the non-symmetry of the experimental breakthrough curve indicates that there are two adsorption mechanisms occurring, and at very different rates. It is expected that chemisorption/chemical reactions proceed much faster than physisorption, and the correct model needs to have those two terms separated.

The Zhang and Cheng model can be summarized in the points below.

- Plug flow assumption, isothermal conditions, and negligible axial dispersion
- Equilibrium assumption is assumed as reactions are instantaneous on the carbon surface
- Mass transfer resistances are negligible, as dissociated ions can travel easily through the water film
- First order reaction kinetics with respect to hydrogen sulfide, and in agreement reaction pathways described in section 2.7
- Linear adsorption isotherm
- Deactivation function for the degeneration (blocking off) of active sites
The model will be used to predict the bed height required, operating life span of the bed and adsorption capacity of the bed. Operating parameters of most importance are bed height $Z$, initial concentration $C_o$, volumetric flow rate $Q$, and bed diameter $D$. 
Chapter 4
Activated Biochar Characterization and Hydrogen Sulfide Adsorption Behavior

4 Activated Biochar Characterization and Hydrogen Sulfide Adsorption Behavior

4.1 Introduction

In the sections below, experimental work performed by Andrew White in his thesis work will be studied and used to validate the Zhang and Cheng model. As experimental data is very hard to replicate and compare, due to the age of the carbon and precursor material changing the model constants. The validity of the model is proved then by linear regression fit (as previously done in Chapter 3), and comparing the behavior of the model to expected trends from experimental observations and literature.

4.2 The Effect of Different Pyrolysis Temperatures

In the pyrolysis step (also known as carbonization) volatile organic components are removed with the use of high temperatures. When these organic components are removed, the carbonaceous skeleton rearranges its structure into graphene layers stacked in random order. This re-arranged structure is the beginning of the desired internal porosity which attributes to the adsorptive capacity of the biochar. The edges of the carbon layers, called actives sites, have higher densities of unpaired electrons and therefore chemisorb more heteroatoms, such as oxygen, hydrogen, nitrogen, sulfur, etc (Bandosz T. J., Activated Carbon Surfaces in Environmental Remediation, 2006). When internal pore structure develops, more of these functional groups at the edge of the carbon layers are exposed and accessible to the adsorbate in the challenge gas. Therefore, the carbonization temperature of the biochar was studied to see its effect on internal porosity and subsequently adsorption capacity.

In White’s experiments, different pyrolysis temperatures of 400°C (BC-1), 500°C (BC-2), 700°C (BC-3), and 800°C were used. Refer to Appendix A for experimental procedure. These different temperatures were selected based on the thermogravimetric analysis (TGA) of the raw precursor material (digestate) in Figure 4.2.1 below, taken from (White, 2010). The TGA curve shows
weight loss as a function of temperature, the first peak at 100°C represents loss of water, the wider peak at ~300°C represents hemicelluloses loss, and the peak at 390°C represents loss of cellulose, followed by the slow loss of lignin (White, 2010). As such, a minimum temperature of 400°C was chosen as the starting point.

![Figure 4.2.1 - Thermogravimetric Analysis of Raw Digestate (White, 2010)](image)

**Figure 4.2.1 - Thermogravimetric Analysis of Raw Digestate (White, 2010)**

It is expected that with higher temperatures, more volatile organic components are removed and greater internal porosity can be achieved. In White’s work, BET analysis was only done on select virgin samples, which are different from samples BC-1 to BC-3 mentioned above as they are spent/used samples. In Table 4.2.1 taken from (White, 2010), the surface area and pore volumes of selected samples can be seen. By comparing virgin samples BC-8 and BC-9, it can be seen that the greatest increase in surface area is through the pyrolysis stage at temperatures greater than 500°C (White, 2010). The increase in surface area is indicative of internal pore development.
Table 4.2.1 - BET Surface Area and Pore Volumes for Selected Samples (White, 2010)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pyrolysis Temperature [°C]</th>
<th>$S_{BET}$ [m$^2$/g]</th>
<th>$V_{TOTAL}$ [cm$^3$/g]</th>
<th>$V_{micro}$ %</th>
<th>$V_{meso}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABC-2</td>
<td>700</td>
<td>317.6</td>
<td>0.2198</td>
<td>72.4</td>
<td>20.5</td>
</tr>
<tr>
<td>BC-8</td>
<td>500</td>
<td>62.1</td>
<td>0.0522</td>
<td>75.5</td>
<td>18.4</td>
</tr>
<tr>
<td>ABC-11</td>
<td>500</td>
<td>249.3</td>
<td>0.1796</td>
<td>68.7</td>
<td>23.8</td>
</tr>
<tr>
<td>BC-9</td>
<td>700</td>
<td>263.6</td>
<td>0.1679</td>
<td>72.2</td>
<td>15.8</td>
</tr>
<tr>
<td>ABC-12</td>
<td>700</td>
<td>291.9</td>
<td>0.2106</td>
<td>72.2</td>
<td>22.1</td>
</tr>
</tbody>
</table>

In dry conditions, adsorption proceeds mainly by physisorption on non-impregnated carbons. However, in this case, some chemisorption can still take place in dry conditions as there are hydroxide salts predisposed on the surface from the digestate precursor material, without having to go through the impregnation step. In wet conditions (discussed further in section 4.4), chemisorption is dominant and greater internal porosity will allow greater accessibility to the active sites by the dissociated hydrogen sulfide ions. Therefore, it is expected that with higher pyrolysis temperatures, greater adsorption capacity of the biochar can be achieved for both wet and dry conditions. This can be seen in Table 4.2.2 below, comparing the different adsorption capacities of the carbon at 30ppm breakthrough concentration. The column was run with the same column conditions as outlined in Appendix A, but with dry air and no column pre-humidification.

Table 4.2.2 - Adsorption Capacity at Different Pyrolysis Temperatures

<table>
<thead>
<tr>
<th>Pyrolysis Temp (°C)</th>
<th>Dry/Humid Inlet Gas</th>
<th>Pre-Humidification</th>
<th>Steam Activation Temp (°C)</th>
<th>Capacity @ 30ppm (mg H2S/g AC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>dry</td>
<td>No</td>
<td>-</td>
<td>0.27</td>
</tr>
<tr>
<td>500</td>
<td>dry</td>
<td>No</td>
<td>-</td>
<td>3.30</td>
</tr>
<tr>
<td>500</td>
<td>dry</td>
<td>No</td>
<td>-</td>
<td>2.58</td>
</tr>
<tr>
<td>850</td>
<td>dry</td>
<td>No</td>
<td>-</td>
<td>24.22</td>
</tr>
</tbody>
</table>

In dry conditions, a more direct correlation between internal porosity and physical adsorption can be studied. Without the water film present, chemisorption via oxidation reactions on the surface...
is limited as only one mechanism can proceed with alkali hydroxides. As such, different pyrolysis temperatures in wet conditions were not tested. In Table 4.2.3 below, it can be found that there is a direct relationship between $K_i$ and pyrolysis temperature. This implies that as pyrolysis temperature increases, physical adsorption increases. As previously concluded, internal porosity increases as pyrolysis temperature increases, therefore, it can also be said that physical adsorption increases as internal porosity increases. This is expected and in agreement with literature (Bandosz T. J., 2006). The same trend is observed for reaction constant $K$ versus pyrolysis temperature. Likewise, with greater internal porosity hydrogen sulfide has access to more carbon surface area resulting in more contact with alkali hydroxide groups. Though XPS analysis was not run on the surface of the sulfur loaded carbons after use, it is expected that no increase in elemental sulfur would be detected in comparison to the virgin sample. XPS analysis should show peaks for sulfides and $Na_2S$ for carbons used in dry conditions.

### Table 4.2.3 - Adsorption Constant and Reaction Constant vs. Pyrolysis Temperature

<table>
<thead>
<tr>
<th>Pyrolysis Temp ($^\circ$C)</th>
<th>Dry/ Humid</th>
<th>Pre- Humidification</th>
<th>Steam Activation Temp ($^\circ$C)</th>
<th>Capacity @ 30ppm (mg H2S/g AC)</th>
<th>$K_d$ [1/s]</th>
<th>$K$ [1/s]</th>
<th>$K_i$ [L gas/g AC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>dry</td>
<td>no</td>
<td>-</td>
<td>0.27</td>
<td>8.71E-03</td>
<td>1.01E+01</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>400</td>
<td>dry</td>
<td>no</td>
<td>-</td>
<td>0.27</td>
<td>1.02E-02</td>
<td>8.17E+00</td>
<td>5.14E-01</td>
</tr>
<tr>
<td>500</td>
<td>dry</td>
<td>no</td>
<td>-</td>
<td>3.30</td>
<td>1.72E-03</td>
<td>2.78E+01</td>
<td>2.52E+00</td>
</tr>
<tr>
<td>500</td>
<td>dry</td>
<td>no</td>
<td>-</td>
<td>2.58</td>
<td>1.37E+03</td>
<td>2.13E+01</td>
<td>2.82E-05</td>
</tr>
<tr>
<td>850</td>
<td>dry</td>
<td>no</td>
<td>-</td>
<td>24.22</td>
<td>6.42E-04</td>
<td>2.89E+01</td>
<td>1.09E+01</td>
</tr>
</tbody>
</table>

Though not included, values of $K$ and $K_i$ were plotted against pyrolysis temperature. No empirical correlation, such as linear relationship, was found. This can be attributed to the decay in adsorption capacity of the carbon with age, further discussed in Section 4.6. It cannot be concluded what relationship $K$ would have as a function of pyrolysis temperature, more work would need to be completed on carbon samples of the same age. As oppose to $K_i$ or $K$ versus pyrolysis temperature, carbon samples for each run should be BET analyzed before use, and $K_i$ or $K$ versus surface area can be studied. In conclusion, $K$ and $K_i$ are expected to vary from sample to sample depending on carbonization parameters and these constants need to be determined from the model before adsorption capacity can be predicted.
4.3 The Effect of Steam Activation

The activation step, which follows the carbonization step, employs an oxidizing agent to attack the carbons located at the edge of the graphite sheets. This results in pores being opened and widened, and the desired micro and mesopore structure is created. Steam was used as the activating agent for the carbonized biochar; refer to Appendix A for procedure. In literature (Bandosz T. J., 2006) (Dalai, Cundall, & De, 2008) (Feng, Kwon, Borguet, & Vidic, 2005) and White’s thesis, it was found that the surface area of the activated carbon was less important than the pore size distribution. Referring back to Table 4.2.1 - *BET Surface Area and Pore Volumes for Selected Samples*, for a comparison of the steam activated samples to non-steam activated samples. Virgin samples BC-8 and ABC-11 were both pyrolysed at 500°C, ABC-11 which was steam activated had greater surface area and percent mesopore contribution. Virgin samples BC-9, ABC-2, and ABC-12 were all pyrolysed at 700°C, steam activated samples ABC-2 and ABC-12 both had greater surface area and greater percent mesopore contribution than BC-9. The increase in surface area after steam activation is an indication of greater porosity of both micro and mesopores.

Filling of the micropores by sulfur or sulfates is the limiting factor for activated biochar capacity. Steijn and Mars found strong sulfur adsorption in pores between 0.5-1nm, which is expected based on the size of sulfur chains and the overlapping of adsorption potential in pores similar in size to the adsorbate molecule (Steijns, Derks, Verloop, & Mars, 1976). When sulfur is adsorbed in such small pores the presence of large polymers is unlikely, and isolated adsorbed sulfur radicals are further oxidized to SO$_2$ and SO$_3$. With higher percent mesopore contribution, it is expected that sulfur chains will form as the pores are larger. Steam activation was also found to increase the presence of elemental sulfur on the surface of the carbon due to sulfate species present before activation being reduced to elemental sulfur. This was also confirmed from XPS analysis conducted by White on different samples, as the ratio of elemental sulfur to sulfate increased after steam activation (White, 2010). From XPS analysis, it was also found that salts such as sodium, potassium, calcium, and/or magnesium would be partially converted to oxide or hydroxide species during steam activation.

Therefore, steam activation will increase adsorption capacity of the carbon in more ways than one. With steam activation it is expected that physical adsorption would slightly increase due to
the increase in carbon porosity. Steam activation would have a greater impact on chemisorption, as greater surface area will allow for more contact of HS⁻ ions with active sites. Furthermore, greater mesopore contribution and elemental sulfur on the carbon surface also increases the autocatalytic polysulfide reaction. Degradation is also expected to slow down as mesopores do not fill up and get blocked up as quickly as micropores. Experiments were done by White comparing activated and non-activated carbon samples from the same digestate batch. In Table 4.3.1 below, it can be seen that physical adsorption constant $K_i$ triples with steam activation, the reaction constant $K$ is almost 20 times greater for the steam activated sample, and the degradation constant $K_d$ is more than four times smaller with steam activation. The samples below were tested with column conditions outlined in Appendix A with wet gas stream.

Table 4.3.1 - Adsorption Constant, Reaction Constant and Degradation Constant with Steam Activation

<table>
<thead>
<tr>
<th>Steam Activation Temp (°C)</th>
<th>Dry/ Humid</th>
<th>Pre-Humid</th>
<th>Pyrolysis Temp (°C)</th>
<th>Capacity @ 30ppm (mg H2S/g AC)</th>
<th>Breakthrough time (s)</th>
<th>$K_d$ [1/s]</th>
<th>$K$ [1/s]</th>
<th>$K_i$ [Lgas/g AC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>humid yes</td>
<td>700</td>
<td>34.45</td>
<td>4778</td>
<td>2.277E-04</td>
<td>2.946E+01</td>
<td>4.856E+01</td>
<td></td>
</tr>
<tr>
<td>850</td>
<td>humid yes</td>
<td>700</td>
<td>313.58</td>
<td>58870</td>
<td>5.434E-05</td>
<td>1.767E+02</td>
<td>1.459E+02</td>
<td></td>
</tr>
</tbody>
</table>

Less can be drawn from comparing constants found for different biochar samples since it is not a like-for-like comparison as pyrolysis temperature, digestate precursor batch, and age of sample are not constants. However, it can be concluded that greater adsorption capacity is achieved with steam activation. Below in Table 4.3.2 is a summary of the adsorption capacity for biochar samples with and without steam activation.
### Table 4.3.2 - Adsorption Capacity and Steam Activation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dry/Humid</th>
<th>Pre-Humid</th>
<th>Pyrolysis Temp (°C)</th>
<th>Steam Activation Temp (°C)</th>
<th>Capacity @ 30ppm (mg H2S/g AC)</th>
<th>Breakthrough time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC2</td>
<td>dry</td>
<td>no</td>
<td>N/A</td>
<td>-</td>
<td>2.05</td>
<td>40</td>
</tr>
<tr>
<td>BC1a</td>
<td>dry</td>
<td>no</td>
<td>400</td>
<td>-</td>
<td>0.27</td>
<td>40</td>
</tr>
<tr>
<td>BC1b</td>
<td>dry</td>
<td>no</td>
<td>400</td>
<td>-</td>
<td>0.27</td>
<td>40</td>
</tr>
<tr>
<td>BC3a</td>
<td>dry</td>
<td>no</td>
<td>500</td>
<td>-</td>
<td>3.30</td>
<td>450</td>
</tr>
<tr>
<td>BC3b</td>
<td>dry</td>
<td>no</td>
<td>500</td>
<td>-</td>
<td>2.58</td>
<td>450</td>
</tr>
<tr>
<td>ABC2a</td>
<td>humid</td>
<td>yes</td>
<td>700</td>
<td>850</td>
<td>113.20</td>
<td>35420</td>
</tr>
<tr>
<td>ABC2b</td>
<td>humid</td>
<td>yes</td>
<td>700</td>
<td>850</td>
<td>127.60</td>
<td>20590</td>
</tr>
<tr>
<td>ABC3a</td>
<td>humid</td>
<td>yes</td>
<td>700</td>
<td>850</td>
<td>313.58</td>
<td>58870</td>
</tr>
<tr>
<td>ABC3b</td>
<td>humid</td>
<td>yes</td>
<td>700</td>
<td>850</td>
<td>283.56</td>
<td>55670</td>
</tr>
<tr>
<td>ABC4</td>
<td>humid</td>
<td>yes</td>
<td>-</td>
<td>850</td>
<td>266.44</td>
<td>48060</td>
</tr>
<tr>
<td>ABC5a</td>
<td>humid</td>
<td>yes</td>
<td>500</td>
<td>850</td>
<td>350.27</td>
<td>63040</td>
</tr>
<tr>
<td>ABC5b</td>
<td>humid</td>
<td>yes</td>
<td>500</td>
<td>850</td>
<td>186.98</td>
<td>59700</td>
</tr>
<tr>
<td>ABC6a</td>
<td>humid</td>
<td>yes</td>
<td>500</td>
<td>850</td>
<td>422.35</td>
<td>88340</td>
</tr>
<tr>
<td>ABC6b</td>
<td>humid</td>
<td>yes</td>
<td>500</td>
<td>850</td>
<td>334.19</td>
<td>36600</td>
</tr>
<tr>
<td>ABC6c</td>
<td>humid</td>
<td>yes</td>
<td>500</td>
<td>850</td>
<td>371.76</td>
<td>61070</td>
</tr>
<tr>
<td>ABC7</td>
<td>humid</td>
<td>yes</td>
<td>500</td>
<td>500</td>
<td>20.01</td>
<td>36600</td>
</tr>
<tr>
<td>ABC8b</td>
<td>humid</td>
<td>yes</td>
<td>500</td>
<td>850</td>
<td>237.66</td>
<td>47420</td>
</tr>
<tr>
<td>ABC8a</td>
<td>humid</td>
<td>yes</td>
<td>500</td>
<td>850</td>
<td>164.49</td>
<td>30970</td>
</tr>
</tbody>
</table>

#### 4.4 The Effect of Humidity

In literature (Pimavera, Trovarelli, Audreussi, & Dolcetti, 1998), it was shown that water plays a key role in the H2S adsorption process. The presence of water increases the capacity of the carbon in two ways:

i) the catalytic reaction takes place in the water phase as oppose to the carbon surface within the pores of the catalyst by dissolving oxygen and H2S in the water film formed

ii) water slows down the degeneration process of activated carbon by promoting deposition of sulfur by mechanically removing sulfur from active sites
In White’s work, experimental runs were done with dry air and no column pre-humidification, then with humid air and no column pre-humidification, and then finally with both humid air and column pre-humidification (Refer to Appendix A for experimental procedure) (White, 2010). It was found that humid air increased the adsorption capacity of the carbon bed, and even greater capacity was achieved with both humid air and pre-humidification. The presence of water, introduced from humid air stream, or pre-humidification, or both, increased the capacity of the carbon by the two mechanisms mentioned above. This can be seen by comparing the adsorption capacity at different operating conditions in Table 4.4.1 below.

Table 4.4.1 - Adsorption Capacity with Dry Air, Humid Air and Pre-Humidification

<table>
<thead>
<tr>
<th>Dry/Humid</th>
<th>Pre-Humid</th>
<th>Pyrolysis Temp (°C)</th>
<th>Steam Activation Temp (°C)</th>
<th>Capacity @ 30ppm (mg H2S/g AC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dry</td>
<td>no</td>
<td>850</td>
<td>-</td>
<td>24.22</td>
</tr>
<tr>
<td>humid</td>
<td>no</td>
<td>850</td>
<td>-</td>
<td>34.24</td>
</tr>
<tr>
<td>humid</td>
<td>yes</td>
<td>850</td>
<td>-</td>
<td>33.01</td>
</tr>
</tbody>
</table>

The advantages of water present is expected to be more effective with pre-humidification of the column, as there is sufficient time for water to diffuse into the internal pores of the activated biochar and condense. After the pre-humidification step, a water film is formed not only on the carbon surface but in the internal pores as well. As such, pre-humidification results in more effective adsorption as it allows for the water-phase reactions to take place on the entire outer surface and internal surface of the carbon right from start-up. Whereas, without pre-humidification, the water film is slowly formed from the humidified air passing through the carbon bed, leading to a lag time before the internal pore surface are accessible to water-phase reactions.

The oxidation of H2S to elemental sulfur can follow many different pathways (as discussed in Chapter 2), however, water and oxygen must be present. Water must be present and the carbon surface must be alkaline in nature for hydrogen sulfide to dissociate into ions, and oxygen must be present to oxidize the intermediate species to elemental sulfur. Therefore, the presence of water greatly increases the chemisorption capacity of the carbon which can be seen by comparing reaction constants between different humidification conditions. In Table 4.4.2,
reaction rate constant $K$ is greater for humid air than dry air with no pre-humidification, $K$ is even greater when column is both fed with humid air and pre-humidified. Contrary, the presence of water film decreases the physical adsorption constant $K_i$ as the adsorption mechanism is shifted to be chemical adsorption dominant as oppose to physical. The formation of a water film covering the entire surface, including internal pores, of each activated carbon particle is important to slowing down the degradation of the activated carbon. It can be seen from the degradation constant $K_d$ that degradation is slower with humid air, and occurs even slower with both humid air and pre-humidification. It can also be concluded that the constants $K$, $K_i$ and $K_d$ are a function of water concentration, and further work needs to be completed to define these correlations.

Table 4.4.2 - Adsorption Constant, Reaction Constant and Degradation Constant at Different Humidification Conditions

<table>
<thead>
<tr>
<th>Dry/Humid</th>
<th>Column Pre-Humidification</th>
<th>Pyrolysis Temp (°C)</th>
<th>Steam Activation Temp (°C)</th>
<th>Capacity @ 30ppm @ 30°C (mg H2S/g AC)</th>
<th>Breakthrough time (s)</th>
<th>$K_d$ [1/s]</th>
<th>$K_i$ [1/s]</th>
<th>$K_d$ [L gas/g AC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>dry no</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>humid no</td>
<td>850</td>
<td>-</td>
<td>24.22</td>
<td>2650</td>
<td>6.42E-04</td>
<td>2.89E+01</td>
<td>1.09E+01</td>
<td>-</td>
</tr>
<tr>
<td>humid Pre-Humid</td>
<td>850</td>
<td>-</td>
<td>34.24</td>
<td>4140</td>
<td>5.62E-04</td>
<td>1.29E+02</td>
<td>9.07E-03</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>33.01</td>
<td>6820</td>
<td>1.09E-03</td>
<td>2.13E+02</td>
<td>0.00E+00</td>
<td></td>
</tr>
</tbody>
</table>

4.5 The Effect of Sulfur Surface Groups

As previously mentioned, elemental sulfur initially present on the carbon surface autocatalyzes the oxidation of hydrogen sulfide in the presence of water. To confirm this, White removed sulfur from an activated bio-char samples using a two stage solvent extraction (experimental procedure included in Appendix A) (White, 2010). Carbon sample was tested in the same column conditions as outlined in Appendix A, and capacity was determined to be 55mg H₂S/g carbon (White, 2010). From analysis of the rate constant versus carbon samples without sulfur washing of the same age (1 day), it was found that $K$ greatly decreased.
4.6 The Effect of Decay

It was found that carbon samples loss activity with age, as decreased adsorption capacity was noticed between samples of the same carbonization, pyrolysis and column parameters. White had plotted the carbon capacity decay as a function of carbon age, and found a linear relationship between sets of carbon pyrolyzed at 500°C and sets of carbon pyrolyzed at 700°C (White, 2010). Both sets of carbons underwent steam activation at 850°C. To limit possible decay from contact with air or moisture, samples were aged in a sealed container with argon and continuous flow of hydrated nitrogen (procedure in Appendix A). In comparison to predicted capacity using the linear relationship, sample ABC-6c had greater capacity than a carbon at 14 days from the linear equation. It should be noted that this sample is an outlier, and this specific batch of activated biochar had greater activity than other samples. Samples ABC-8b and ABC-8a aged 10 and 15 days respectively, had lower capacity than predicted from the linear equation. In Table 4.6.1 below, it can be seen between samples ABC-8b and ABC-8a that degradation constant $K_d$ and adsorption constant $K_i$ are fairly constant, whereas, reaction rate constant $K$ decreased by more than half. This indicates that the decay in adsorption capacity is associated with loss of active species such as hydroxides. Loss of hydroxides could occur through surface reaction with carbon to form carbonates. More testing and analysis would be required before the mechanism by which active species are loss can be confirmed.

Table 4.6.1 - Reaction Rate Constant without Sulfur Surface Group

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pyrolysis Temp (°C)</th>
<th>Steam Activation Temp (°C)</th>
<th>Capacity @ 30ppm (mg H2S/g AC)</th>
<th>Breakthrough time (s)</th>
<th>$K_d$ [1/s]</th>
<th>$K$ [1/s]</th>
<th>$K_i$ [L gas/g AC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABC6a</td>
<td>500</td>
<td>850</td>
<td>422.35</td>
<td>88340</td>
<td>5.68E-05</td>
<td>9.47E+02</td>
<td>1.38E+02</td>
</tr>
<tr>
<td>Without Sulfur Groups</td>
<td>500</td>
<td>850</td>
<td>54.66</td>
<td>13960</td>
<td>2.60E-04</td>
<td>2.36E+02</td>
<td>2.39E+01</td>
</tr>
</tbody>
</table>
Table 4.6.1 - Reaction Rate vs. Activated Biochar Age

<table>
<thead>
<tr>
<th>Sample</th>
<th>Age</th>
<th>Capacity @ 30ppm (mg H2S/g AC)</th>
<th>Breakthrough time (s)</th>
<th>$K_d$ [1/s]</th>
<th>$K$ [1/s]</th>
<th>$K_i$ [L gas/g AC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABC6c</td>
<td>14 days</td>
<td>334.19</td>
<td>36600</td>
<td>4.03E-05</td>
<td>2.27E+01</td>
<td>2.30E+02</td>
</tr>
<tr>
<td>ABC8b</td>
<td>10 days</td>
<td>237.66</td>
<td>47420</td>
<td>6.20E-05</td>
<td>1.00E+02</td>
<td>1.29E+02</td>
</tr>
<tr>
<td>ABC8a</td>
<td>15 days</td>
<td>164.49</td>
<td>30970</td>
<td>6.01E-05</td>
<td>3.60E+01</td>
<td>1.31E+02</td>
</tr>
</tbody>
</table>

4.7 Summary

The following conclusions were drawn from discussions above:

- Increased pyrolysis temperature increased pore development, resulting in increased adsorption capacity via both physisorption and chemisorption.

- $K$, $K_i$ and $K_d$ are a function of pyrolysis temperature. $K$ and $K_i$ increased, whereas $K_d$ decreased with increased pyrolysis temperature.

- Steam activation increased surface area, percent mesopore contribution, and initial elemental sulfur on carbon surface, resulting in increased overall adsorption capacity. Slight increase in physisorption was detected, and a significant increase in chemisorption detected, and a decrease in degradation rate.

- $K$, $K_i$ and $K_d$ are related to steam activation. $K$ and $K_i$ increased, whereas $K_d$ decreased with steam activation.

- Using humid air in the challenge gas increased the adsorption capacity, further capacity increase was detected with column pre-humidification. Adsorption mechanisms shifted to chemisorption dominant over physisorption with pre-humidification and humid air, degradation also slowed down.

- $K$, $K_i$ and $K_d$ are a function of humidity. $K$ and $K_i$ increased, whereas $K_d$ decreased with humid air and column pre-humidification.
• Elemental sulfur initially present on the carbon surface is important to the adsorption capacity of the carbon. Decreased capacity was determined when sulfur was removed, consequently, K also decreased.

• Carbon samples aged with time even in an air-tight environment. Decrease in K implies active species such as hydroxides could be lost through surface reactions with carbon to form carbonates.
Chapter 5
The Effect of Different Operating Parameters – Case Studies

5 The Effect of Different Operating Parameters – Case Studies

5.1 Introduction

In the following sections, the model is tested for sensitivity towards different operating parameters. One parameter at a time will be varied to show its effect on adsorption behaviour. The sensitivity analysis could be done based on any activated biochar batch, it was chosen to run the analysis based on experimental run 04/08/2010-S1 or ABC3a. This experimental run was chosen because the carbon was made at the optimized carbon pyrolysis and activation parameters. Compared to other activated biochars made using the same parameters, it had approximately the average capacity and breakthrough time. Therefore, the basis for the sensitivity analysis is ABC3a, as it is a good representative of carbon behaviour for biochars pyrolysed at 700°C and activated at 850°C.

5.2 Carbon Bed Length

In Figure 5.2.1 below, it can be observed with decreasing bed length it is expected that adsorption capacity of the unit will decrease; this is expected as less activated carbon will be present and the residence time is smaller. Likewise, an earlier breakthrough is also expected for shorter bed lengths. It should be noted that at a low enough bed length, breakthrough occurs at time zero indicating that more carbon/greater bed length is required for effective removal. By running case studies, a specific bed length can be found that matches the needs of the application. As previously discussed in Chapter 1, it is necessary that the outlet concentration does not exceed 200ppm if the purified biogas will be combusted in an engine to produce electricity. Since the model is fairly sensitive to bed length, this design parameter can be adjusted optimize the operating life span for 200ppm outlet concentration.
5.3 Bed Porosity

In Figure 5.3.1 below, adsorption capacity of the column is expected to decrease as porosity increase. This behaviour is expected as less activated carbon is present in more porous beds. The model used is clearly not very sensitive to porosity changes. However, lower porosity should result in a greater pressure drop through the bed which will affect the physical uptake (physisorption) of hydrogen sulphide. With increased pressure drop across the bed, the tail end of the bed will be at a lower pressure which will decrease the physical adsorption uptake at this point. The model does not account for this behaviour and a relationship between pressure drop (or average bed pressure) and adsorption isotherm constant ($K_i$) needs to be found with future work and included in the model. The model also does not account for the possible effect of axial flow (back flow) in the case that porosity is too high. With a very porous bed, there may no longer be plug flow and wall effects will cause axial dispersion and mass transfer resistance, which will lower the mass transfer rate at the carbon/fluid interface. As such, it is important that the porosity of the bed have a lower and upper bound.
In Figure 5.4.1 below, the model shows that with increased bed diameter, there will be an increase in adsorption capacity since more activated carbon is present in the bed. Like bed porosity, it is important to note that with very large bed diameter, plug flow may no longer be a valid assumption and axial flow, axial dispersion and mass transfer resistance effects need to be taken into account. As all these aforementioned phenomena decrease transport efficiency, it is important to bound the bed diameter to maintain plug flow. This bound must be included in the model and should be determined in future work to fully define the model.
5.4.1 - The Effect of Varying Bed Diameter on Adsorption Capacity

5.5 Superficial Velocity and Volumetric Flow Rate

From Figure 5.5.1, it can be seen that the model is not very sensitive to variations in superficial velocity. Superficial velocity may seem to be an important parameter to study, however, it is not really an adjustable parameter as it is linked to too many operating variables. For example, changing temperature, pressure, volumetric flow rate, bed diameter, initial concentration and bed porosity will all affect superficial velocity. As such, studying the effect of varying superficial velocity gives little valuable insight. Therefore, volumetric flow rate will be varied as it is a directly controllable operating parameter. As expected, the model predicted that with increasing volumetric flow rate, breakthrough occurs earlier and adsorption capacity remains the same. As the rate of introduction of contaminants increases, the active sites are blocked off quicker. As the model is not very sensitive to changes in superficial velocity/flow rate, this indicates that the adsorption of hydrogen sulphide is not limited by kinetics.
5.6 Initial Concentration

In Figure 5.6.1 below, it can be seen that with increased inlet concentration, breakthrough was predicted to occur earlier. It should be noted that a relationship between inlet concentration and deactivation constant ($K_d$) needs to be further studied. In section 3.4.7 in the derivation of the deactivation relationship, it is stated that the solution is applicable for constant inlet concentration. As $K_d$ is a rate constant for the rate at which the active sites on the surface of the activated carbon are being used up, it is expected to change with inlet concentration. The relationship for the deactivation is derived based on the probability that H$_2$S will collide with an active site. As such, it is expected that $K_d$ will increase with increasing inlet concentration as more H$_2$S particles present will result in more frequent active site collisions on the carbon surface. The set of curves below were generated assuming the relationship of $K_d$ to $C_0$ to be directly proportional. That is $K_d = aC_0$, where $a$ is a constant. However, this relationship is yet to
be validated and future experiments must be done to validate the correlation and define the relationship between $K_d$ and $C_0$.

Figure 5.6.1 - Effect of Varying Inlet Concentration on Adsorption Capacity

5.7 Effect of Varying Degradation Constant on Shape of Breakthrough Curve

In Figure 5.7.1 below, it was found that by varying the deactivation constant, the shape of the breakthrough curve could be changed. With a lower deactivation constant, breakthrough occurs later and the rate at which the carbon bed reaches the maximum capacity is much faster (bed is degrading faster). As deactivation rate is representative of the rate at which the active sites are being blocked/consumer, deactivation is a function of both chemical and physical adsorption. It can also be concluded that $K_d$ is a function of many different parameters.
5.8 Effect of Varying Kinetic Constant on Shape of Breakthrough Curve

From Figure 5.9.1 below, it was found that by varying only the kinetic constant, a shift in the breakthrough curve is predicted. Therefore, with a slower reaction rate breakthrough occurs earlier. In other words, a decrease in chemisorption reduces the overall adsorption capacity of the column.
Figure 5.8.1 - Effect of Varying K on Shape of Breakthrough Curve

5.9 Effect of Varying Adsorption Constant

In Figure 5.9.1 below, it was found that by varying Ki, much like varying K, there was no change in the shape of the breakthrough curve but only a shift in breakthrough time. It was also found that the model was less sensitive to changes in Ki than K, which is an indication that the uptake of H₂S by the studied activated carbon is chemical adsorption dominant.
5.10 Summary

Below is a summary of the capabilities of the model developed:

- For given batch of activated carbon, pyrolysed and activated using the same parameters, and having the same age, the following can be accurately predicted after the parameters of the model are found:
  - Breakthrough capacity
  - Breakthrough time
  - Life span of adsorber bed
Given that temperature, humidity, and oxygen concentration remain constant.

- The following parameters can also be adjusted to achieve a desired bed capacity or life span of the adsorber bed.
  - Volumetric flow
  - Bed length
  - Bed diameter

Below is a summary of relationships that need to be defined in future work:

- The relationship between $K_d$ and $C_0$ needs to be defined and validated
- Bed diameter and porosity need to be bounded to maintain plug flow

Below are some limitations to the model that need to be considered and addressed in future work:

- The effect of temperature was not studied in the sensitivity analysis as the unit will be operated at ambient temperatures. Also, since the carbon surface is alkaline in nature, the ignition temperature is lowered which could pose a self ignition hazard. Therefore, it is not desirable to operate at high temperature. That being said, if temperatures were raised within the safe limits, it is expected to increase the rate of physical and chemical adsorption as kinetics would be faster, but also increase deactivation rate.

- Water concentration is not incorporated into the model yet. But from Section 4.4 it is clear that $K$, $K_i$ and $K_d$ are related to relative humidity. It is expected that the effect of water is beneficial to a certain optimum, where the entire carbon surface maintains a constant thin water film. When the column is pre-humidified, a thin water film is formed on the carbon surface and within the pores. Feeding humid air (saturated with water) into the column ensures that the water is not evaporated off the carbon surface as the gas passes through the column by replenishing as required. Therefore, if two conditions below are met, then the model parameters ($K$, $K_i$ and $K_d$) are expected to not vary with changes in water concentration:
column is pre-humidified

sufficient humid air is supplied to maintain the carbon surface water film

It should also be noted that excessive water can cause overloading and introduce undesired mass transfer resistance. Future work should be completed to bound the minimum and maximum amount of water concentration in the humid air stream.

The effect of oxygen/air concentration is not incorporated into the model yet. It is expected that oxygen is beneficial to a certain optimum, as it is needed for the intermediate sulfur species to be oxidized to elemental sulfur. The optimum will be approximately the stoichiometric ratio of O₂ required for all the chemical reactions taking place on the carbon surface.
Chapter 6
Scale-Up and Capital Cost Estimate

6 Scale-Up and Capital Cost Estimate

6.1 Introduction

As there are many cattle farms in Ontario ranging in size from small to large, and therefore in biogas potential, the scale-up analysis and capital cost estimate will be done for two cases. The first case being a small cattle farm of 52 animals (lower spectrum) and the second being a larger cattle farm with 2,196 animals (Statistics Canada, 2001, 2006). A simple scale-up will be explained in the section below to demonstrate the models ability to be scaled-up and used for design.

6.2 Scale-Up

To perform a scale-up of the lab size adsorber, the loading rate of the actual unit is required with the inlet concentration of the gas. An average of 2.02 m³ biogas/animal-day is used from an average of literature values (Burke, 2001) (Nelson & Lamb, 2002) (Ontario Ministry of Agriculture) (U.S. Environmental Protection Agency, 2009). In Table 6.2.1 below, the biogas potential for the small and large scale farm are listed.

<table>
<thead>
<tr>
<th></th>
<th>Small Scale</th>
<th>Large Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of animals</td>
<td>52</td>
<td>2196</td>
</tr>
<tr>
<td>Biogas Produced (m³/day)</td>
<td>105</td>
<td>4436</td>
</tr>
</tbody>
</table>

Plug flow is maintained if a certain ratio of bed diameter to catalyst diameter is not exceeded. However, this is not known because the catalyst diameter is not known. Therefore, the diameter/length ratio of the unit will be locked for this scale-up from the experimental model. The same inlet concentration of 450 ppm of hydrogen sulfide, used in experiments, will be used in the scale-up analysis. The value of $K_d$ is expected to change with inlet concentration, but there is no data for estimating $K_d$ as a function of inlet concentration. As anaerobic digester system retention time can range from one week to up to one month, it will be estimated that the adsorber
bed will need to last at least three weeks before fresh activated carbon is required. The system will be operated using two beds in series, once the first bed is saturated the second bed becomes the first bed. The saturated bed is loaded with fresh carbon and becomes the second bed. This cycle allows for the maximum usage of the carbon bed capacity. Therefore, the maximum allowable outlet concentration is the inlet concentration. In Table 6.2.2 below, are the values inputted into the model to obtain the size of the unit.

**Table 6.2.2 - Parameters Input into Model for Scale-Up**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Small Scale</th>
<th>Large Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Concentration of H$_2$S [g/L]</td>
<td>6.258E-04</td>
<td>6.258E-04</td>
</tr>
<tr>
<td>Maximum allowable outlet concentration of H$_2$S [g/L]</td>
<td>6.258E-04</td>
<td>6.258E-04</td>
</tr>
<tr>
<td>$Q$ [L/s]</td>
<td>0.35</td>
<td>51.34</td>
</tr>
<tr>
<td>$K_d$ [s$^{-1}$]</td>
<td>5.469E-05</td>
<td>5.469E-05</td>
</tr>
<tr>
<td>$K$ [s$^{-1}$]</td>
<td>1.797E+02</td>
<td>1.797E+02</td>
</tr>
<tr>
<td>$K_i$ [g carbon/g H$_2$S]</td>
<td>1.459E+02</td>
<td>1.459E+02</td>
</tr>
<tr>
<td>Length/Diameter ratio</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Life span (days)</td>
<td>21</td>
<td>21</td>
</tr>
</tbody>
</table>

Therefore, the dimensions and volume of the unit is summarized in the table below if the carbon bed needs to have a three week life span.

**Table 6.2.3 - Dimensions of Adsorber Column**

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Small Scale</th>
<th>Large Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (m)</td>
<td>0.26</td>
<td>1.36</td>
</tr>
<tr>
<td>Height (m)</td>
<td>1.30</td>
<td>6.80</td>
</tr>
<tr>
<td>Volume (m$^3$)</td>
<td>0.08</td>
<td>9.88</td>
</tr>
</tbody>
</table>
6.3 Capital Cost Estimate

The following correlations and coefficients are taken from equations and tables in (Turton, Bailie, Whiting, & Shaeiwitz, 2003). All data is from the mid-1996, for which CEPCI = 382. The purchase cost \((C_p)\) of equipment assuming ambient operating temperature and carbon steel construction can be estimate from the following equation,

\[
\log_{10} C_p = K_1 + K_2 \log_{10} A + K_3 (\log_{10} A)^2 \quad (6.3.1)
\]

where \(K_1, K_2,\) and \(K_3\) are correlation coefficients, \(A\) is the size parameter which is the length of the vessel (m).

The bare module cost \((C_{BM}^0)\) and the bare module factor \((F_{BM}^0)\) can be calculated using the following equation,

\[
C_{BM}^0 = C_p F_{BM}^0 = C_p (B_1 + B_2 F_M F_p) \quad (6.3.2)
\]

where \(B_1, B_2\) are correlation coefficients, \(F_M\) is the material factor, and \(F_p\) is the pressure factor.

The pressure factor \((F_p)\) for vertical vessels is given by the following correlation.

\[
F_p = 0.5416 + 0.6838 \log_{10} P + 0.2970 (\log_{10} P)^2 + 0.0235 (\log_{10} P)^6 \\
+ 0.0020 (\log_{10} P)^8 \quad \text{where} \ 3.7 < P < 400 \text{bar} \quad (6.3.3)
\]

\[
F_p = 1, \quad \text{where} \ -0.5 < P < 3.7 \text{bar} \quad (6.3.4)
\]

\[
F_p = 1.25, \quad \text{where} \ P < -0.5 \text{bar} \quad (6.3.5)
\]

Therefore, since the unit will be operated at ambient pressure \(F_p = 1\).

The material of construction factor can be taken from the following table.
Table 6.3.1 - Material of Construction Factor

<table>
<thead>
<tr>
<th>Material of Construction</th>
<th>$F_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon steel</td>
<td>1.0</td>
</tr>
<tr>
<td>Stainless steel clad</td>
<td>2.5</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>4.0</td>
</tr>
<tr>
<td>Nickel clad</td>
<td>4.5</td>
</tr>
<tr>
<td>Nickel</td>
<td>9.8</td>
</tr>
<tr>
<td>Titanium clad</td>
<td>4.9</td>
</tr>
<tr>
<td>Titanium</td>
<td>10.6</td>
</tr>
</tbody>
</table>

Stainless steel clad will be used at material of construction as for the ambient operating temperature, stainless steel is compatible to exposure to hydrogen sulfide, water, carbon dioxide, water, sulfides, and sulfates. Therefore, the material factor is 2.5.

For vertical vessels, $B_1 = 2.50$ and $B_2 = 1.72$. For the two cases mentioned above, Table 6.3.2 below summarize the correlation coefficients used for the purchase cost of the vessels.

Table 6.3.2 - Correlation Coefficients for Purchase Cost of Vessel

<table>
<thead>
<tr>
<th></th>
<th>Case 1</th>
<th>Case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (m)</td>
<td>0.26</td>
<td>1.36</td>
</tr>
<tr>
<td>$K_1$</td>
<td>3.3392</td>
<td>3.7559</td>
</tr>
<tr>
<td>$K_2$</td>
<td>0.5538</td>
<td>0.6361</td>
</tr>
<tr>
<td>$K_3$</td>
<td>0.2851</td>
<td>0.1069</td>
</tr>
<tr>
<td>$L_{min}$ (m)</td>
<td>1.2</td>
<td>3.0</td>
</tr>
<tr>
<td>$L_{max}$ (m)</td>
<td>16</td>
<td>41</td>
</tr>
</tbody>
</table>

Therefore, using equation 6.1 the purchase cost for the small vessel would be $2,551 and the large vessel would be $22,885. Plugging all values into equation 6.2, the bare module cost for the small vessel is $17,347 and the large vessel bare module cost is $155,618. The CEPCI index for
2012 is 520.9, therefore, the final bare module cost for the small column is $23,655 and for the large column it is $212,203. As two columns would be operated in series, the final bare module cost for the small scale system is $47,310 and $424,406 for the large scale system. The cost estimate given is based on a custom design unit, which would be more expensive. However, it is not necessarily required to have a custom designed unit. Given the dimensions of an “off-the-shelf” unit, the bed adsorption capacity and lifespan can be calculated to verify if the unit will meet the needs of the application. The biggest limitation to “off-the-shelf” units would be the diameter of the column, as plug flow should be maintained.
Chapter 7
Conclusion and Future Work

7 Conclusion and Future Work

7.1 Conclusion

- The Zhang and Cheng model can be used to model the adsorption of hydrogen sulfide by activated carbon made from anaerobic digestate. The model assumes the following:
  - Plug flow assumption, isothermal conditions, and negligible axial dispersion
  - Equilibrium assumption is assumed as reactions are instantaneous on the carbon surface
  - Mass transfer resistances are negligible, as dissociated ions can travel easily through the water film
  - First order reaction kinetics with respect to hydrogen sulfide
  - Linear adsorption isotherm
  - Exponential decay function for the degeneration (blocking off) of active sites

- For given batch of activated carbon, pyrolysed and activated using the same parameters, and having the same age, the following can be accurately predicted after the parameters of the model are found:
  - Breakthrough capacity
  - Breakthrough time
  - Life span of adsorber bed

  Given that temperature, humidity, and oxygen concentration remain constant.

- The following parameters can also be adjusted to achieve a desired bed capacity or life span of the adsorber bed.
  - Volumetric flow
  - Bed length
Bed diameter

- Operating parameters of most importance are bed height \( Z \), initial concentration \( C_0 \), volumetric flow rate \( Q \), and bed diameter \( D \).

- Increased pyrolysis temperature increased pore development, resulting in increased adsorption capacity via both physisorption and chemisorption.

- Steam activation increased surface area, percent mesopore contribution, and initial elemental sulfur on carbon surface, resulting in increased overall adsorption capacity. Slight increase in physisorption was detected, and a significant increase in chemisorption detected, and a decrease in degradation rate.

- Using humid air in the challenge gas increased the adsorption capacity, further capacity increase was detected with column pre-humidification. Adsorption mechanisms shifted to chemisorption dominant over physisorption with pre-humidification and humid air, degradation also slowed down.

- Elemental sulfur initially present on the carbon surface is important to the adsorption capacity of the carbon. Decreased capacity was determined when sulfur was removed.

- Carbon samples aged with time even in an air-tight environment.

### 7.2 Future Work

Below is a summary of future work to be completed:

- The relationship between \( K_d \) and \( C_0 \) needs to be defined and validated
- Bed diameter and porosity need to be bounded to maintain plug flow
- The effect of temperature was not studied in the sensitivity analysis as the unit will be operated at ambient temperatures. However, it would be of interest to study the process at a range of temperatures.
- Water concentration was not incorporated into the model yet. Correlations between constants \( K \), \( K_i \) and \( K_d \) to relative humidity need to be developed. It should also be noted that excessive water can cause overloading and introduce undesired mass transfer
resistance. Future work should be completed to bound the minimum and maximum amount of water concentration in the humid air stream.

- The effect of oxygen/air concentration is not incorporated into the model yet. Correlations between constants $K$, $K_i$ and $K_d$ to oxygen concentration need to be developed.
References


Appendix A

Introduction

The experimental set-up and experimental procedures were taken from White (White, 2010) who developed and executed the experimental work.

Experimental Set-Up

Below is the diagram explaining the thermal treatment apparatus, adapted from (White, 2010)
Below is the diagram for the hydrogen sulfide adsorption apparatus, adapted from (White, 2010).

Experimental Procedure

Thermal Treatment

1) Bio-char and activated biochar were made from solid material remaining after anaerobic digestion of diary manure. The digestate was filter pressed and stored in a freezer between -10°C and -20°C.

2) 30-40g of digestate material was placed in a quartz tube which had a fritted disk at the bottom to support the sample. The quartz tube was placed in an electric carbolite tube furnace.

3) Samples were brought up to various temperatures (400°C, 500°C, 700°C) with a downwards flow of 50mL/min of nitrogen to remove volatile organic species.
4) Samples were held at high temperatures for an hour after oven temperature reached steady state.
5) Oven was then turned off and samples allowed to cool overnight with 50mL/min of nitrogen flowing through.
6) Samples were then removed and weighed.
7) Activated biochar samples were made the same way following steps 1-4. Then the samples were heated to 850°C and held for another hour, with a downward flow of 250mL/min of hydrated nitrogen which had been passed through the water bubbler.
8) After one hour, the oven was turned off and activated biochar samples were cooled while maintaining nitrogen flow rate. Once oven temperature cooled to 500°C, nitrogen flow was adjusted to 50mL/min of dry nitrogen.
9) Oven was cooled overnight before samples were removed.

Hydrogen Sulfide Adsorption

1) Samples were hand ground using a mortar and pestle
2) Grounded samples were packed 5cm high in a glass tube with an internal diameter of 1.1cm; fritted disks were placed both below and above sample for support.
3) Column was connected to Aalborg GFC mass flow controllers.
4) Column was pre-humidified by passing 250mL/min of nitrogen through a water bubbler overnight.
5) After pre-humidification, flow rate of nitrogen was adjusted to 238mL/min, still passing through the water bubbler.
6) In addition to the nitrogen flow, 7.5mL/min of hydrogen sulfide from a cylinder containing 1.5% nitrogen was blended into the gas stream, as well as 5.0mL/min air.
7) The concentration of hydrogen sulfide in the gas stream was 450ppm, air concentration 2%, and total gas flow rate of 250mL/min.
8) Hydrogen sulfide detector has a maximum limit of 500ppm.
9) The outlet concentration of hydrogen sulfide was measured using an Industrial Scientific GadBadge Pro electrochemical hydrogen sulfide detector (P/N 18100060-2).
10) Once outlet concentration reached 100ppm, gas flows were shut off.
11) Carbon was removed and weighed.

Aging Carbon Samples

1) Samples were stored in polypropylene bottles on a lab bench.
2) Samples were aged in a sealed container with argon and a continuous flow of 25mL/min of hydrated nitrogen.

Removing Sulfur Groups

1) A sample of 0.78672g of ABC-10 was washed with 5mL of carbon disulfide.
2) This value was used as it represents the amount of carbon disulfide that would be needed if the entire mass of samples was sulfur.
3) After washing with carbon disulfide, the sample was then washed with 20mL of chloroform to remove the carbon disulfide.

4) The sample was dried for four hours under vacuum filtration conditions.
Appendix B

A first-order deactivation reaction is assumed and the deactivation rate equation is:

\[ \frac{\partial \phi}{\partial t} = K_d \phi \]

where \( t \) is time (s), \( \phi \) is the deactivation function (dimensionless), and \( K_d \) (s\(^{-1}\)) is the deactivation rate constant. Given the initial condition, when \( t = 0 \), then \( \phi = 1 \), and taking the derivative the expression below is obtained.

\[ \phi = e^{-K_dt} \quad (1) \]

The chemical reaction also follows a first-order reaction and the rate equation is:

\[ R = KC \phi = KCe^{-K_dt} \quad (2) \]

where \( R \) is the reaction rate (g/Ls), \( K \) is the reaction rate constant (s\(^{-1}\)), \( C \) is the adsorbate concentration in the gas stream (g/L). Assuming that the bed dynamics follow ideal plug flow with no axial dispersion, and isothermal conditions, then the superficial gas velocity is kept constant and the continuity equation of the fixed bed adsorber is as follows:

\[ \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + \frac{1 - \varepsilon}{\varepsilon} \rho \frac{\partial q}{\partial t} + R = 0 \quad (3) \]

where \( u \) is superficial velocity (dm/s), \( x \) is the distance from the bed inlet (dm), \( \varepsilon \) is bed porosity (dimensionless), \( q \) is the adsorbate concentration in the carbon (g adsorbate/g carbon), and \( \rho \) is the bulk density of the carbon (g/dm\(^3\)).

The physical adsorption is characterized by a linear isotherm as at small concentrations, the Langmuir isotherm is linear (Zhang & Cheng, 2000).

\[ q = K_l C \quad (4) \]

Then taking the derivative with respect to time of equation (4), the following expression is obtained,
\[
\frac{\partial q}{\partial t} = K_i \frac{\partial C}{\partial t} \quad (5)
\]

where \(K_i\) is the adsorption constant in \((\text{L gas/g carbon})\).

Therefore, plugging expression (5) into equation (3) the expression below is obtained.

\[
\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + \frac{1 - \varepsilon}{\varepsilon} \rho K_i \frac{\partial C}{\partial t} + R = 0 \quad (6)
\]

Rearranging,

\[
\left(1 + \frac{1 - \varepsilon}{\varepsilon} \rho K_i \right) \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = -R
\]

\[
\alpha \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = KC e^{-K_i t} \quad (7)
\]

where \(\alpha = 1 + \frac{K_i \rho (1-\varepsilon)}{\varepsilon} \).

The boundary condition and initial conditions are below.

- At \(x = 0, \ t > 0, \ C = C_0\)
- At \(t = 0, \ x > 0, \ C = 0\)

Using method of characteristics, where

\[
C(x, t) = C(x, t(x)) \quad (8)
\]

then,

\[
\frac{dC}{dx} = \frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} \frac{dt}{dx} \quad (9)
\]

Dividing equation (7) by \(u\) and equating to (9),

\[
\frac{\alpha \partial C}{u \partial t} + \frac{\partial C}{\partial x} = \frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} \frac{dt}{dx} \quad (10)
\]

Therefore,
\[ \frac{\partial t}{\partial x} = \frac{\alpha}{u} \rightarrow x = \frac{u}{\alpha} t + \zeta \rightarrow t = \frac{\alpha}{u} (x - \zeta) \quad (11) \]

where \( \zeta \) is a constant. Boundary and initial conditions can be written as,

- At \( x = 0 \), \( t = -\alpha/u^* \zeta \), \( C = C_0 \)
- At \( t = 0 \), \( x = \zeta \)

From (10), (9), and (7) the following relationship is also drawn.

\[ \frac{dC}{dx} = -\frac{K}{u} C e^{-K_d t} \quad (12) \]

Integrating (12),

\[ \int_{C_0}^{C} \frac{1}{C} dC = -\frac{K}{u} \int_0^x e^{-K_d t} \, dx \]

and plugging in expression (11) for \( t \),

\[ \int_{C_0}^{C} \frac{1}{C} dC = -\frac{K}{u} \int_0^x e^{-K_d \left[ \frac{x - \zeta}{u} \right]} \, dx \]

\[ \ln \left( \frac{C}{C_0} \right) = -\frac{K}{u} \exp \left( \frac{K_d}{u} \zeta \right) \int_0^x e^{-\frac{K_d}{u} x} \, dx \]

\[ \ln \left( \frac{C}{C_0} \right) = -\frac{K}{u} \exp \left( \frac{K_d}{u} \zeta \right) \left[ -\frac{u}{K_d} \exp \left( -\frac{K_d}{u} x \right) \right]_0^x \]

\[ \ln \left( \frac{C}{C_0} \right) = -\frac{K}{u} \exp \left( \frac{K_d}{u} \zeta \right) \left[ -\frac{u}{K_d} \exp \left( -\frac{K_d}{u} x \right) \right]_0^x \]

\[ \ln \left( \frac{C}{C_0} \right) = \frac{K}{K_d} \exp \left( \frac{K_d}{u} \zeta \right) \left[ \exp \left( -\frac{K_d}{u} x \right) - 1 \right] \]

From expression (11), \( \zeta = x - tu/\alpha \), plugging into the above expression, the expression below is obtained.
\[ l \ln \left( \frac{C}{C_0} \right) = \frac{K}{K_d \alpha} \exp \left( \frac{K_d \alpha}{u} \left( x - \frac{u}{\alpha} t \right) \right) \left[ \exp \left( - \frac{K_d \alpha}{u} x \right) - 1 \right] \]

Simplifying and rearranging.

\[ l \ln \left( \frac{C}{C_0} \right) = \frac{K}{K_d \alpha} \exp(-K_d t) \left[ 1 - \exp \left( \frac{K_d \alpha}{u} x \right) \right] \quad (13) \]

The solution above, (13), can be linearized and re-arranged into the following.

\[ \ln \ln \frac{C_0}{C} = \ln \left[ 1 + \frac{K \alpha}{K_i \rho(1 - \varepsilon)} \right] - K_d t + \ln \left\{ e^{\frac{K_d x}{u}} \frac{1}{1 + \frac{K_i \rho(1 - \varepsilon)}{\varepsilon}} - 1 \right\} \quad (14) \]

If the bed height \( x \) is constant (\( x = L \)), the breakthrough curve can be linearized and written as:

\[ \ln \ln \frac{C_0}{C} = a - K_d t \quad (15) \]

where,

\[ a = \ln \frac{K}{K_d \alpha} + \ln \left( e^{\frac{K_d \alpha x}{u}} - 1 \right) \quad (16) \]

\[ \alpha = 1 + \frac{K_i \rho(1 - \varepsilon)}{\varepsilon} \quad (17) \]

The constants \( K, K_i \) and \( K_d \) are solved in the following manner.

From the plot of \( \ln \ln (C_0/C) \) versus time, the slope can be used to find \( K_d \), from the y-intercept the value of \( a \) can be found. However, \( K \) and \( K_i \) can not be found from (16) as there are two unknowns and one equation.

Therefore, the finite difference method is used to write equation (7) in the following form.

\[ \alpha \left( \frac{C_{i,j} - C_{i-1,j}}{\Delta t} \right) + u \left( \frac{C_{i,j} - C_{i,j-1}}{\Delta x} \right) + KC_{i,j}e^{-K_d t_i} = 0 \quad (18) \]
If breakthrough curve data is used to find the constants, then \( j = L \).

\[
\alpha \left( \frac{C_{i,L} - C_{i-1,L}}{\Delta t} \right) + u \left( \frac{C_{i,L} - C_{i,L-1}}{\Delta x} \right) + K C_{i,L} e^{-K_d t_i} = 0 \quad (19)
\]

From re-arranging equation (16), an expression for \( K \) can be obtained.

\[
K = \exp \left( y_{\text{intercept}} - \ln \left[ \exp \left( K_d \alpha \frac{L}{u} \right) - 1 \right] \right) \alpha K_d \quad (20)
\]

\( C_{i,j=L} \) matrix is filled out using step size of \( \Delta x = 0.001 \text{dm} \) and \( \Delta t = 10 \text{s} \). \( C_{i,L} \) matrix can be filled using equation (15), value of \( a \) and \( K_d \) are the slope and \( y \)-intercept found from the linear regression of experimental data.

Before \( C_{i,L-1} \) can be calculated, an initial guess for the value of \( \alpha \) is needed, \( K \) is then calculated using equation (20). \( C_{i,L-1} \) matrix is filled using equations (15) and (16). The value of \( K_d \) was found from linear regression on experimental breakthrough curve, and value of \( a \) is calculated using equation (16) with \( x = L - 0.001 \text{dm} \).

One \( C_{i,L} \) and \( C_{i,L-1} \) matrices are filled, these values are filled into the mass balance equation (19) for every point \( i \). Using quadratic estimates, forward derivatives, and conjugate search method in Excel solver, the value of \( \alpha \) was iterated until \( 1\times10^{-7} \) convergence was obtained at all points.

The constraints below were also set-up in the solver, both of which are intuitive.

\[
\left( \frac{C_{i,L} - C_{i,L-1}}{\Delta x} \right) \bigg|_{x=L} < 0
\]

\[
\alpha \geq 1
\]

From the value of \( \alpha \), the value of \( K_i \) can be found from equation (17).
<table>
<thead>
<tr>
<th>Name</th>
<th>R2</th>
<th>Notes</th>
<th>Kd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chen</td>
<td>0.954</td>
<td>Steam</td>
<td>0.911</td>
</tr>
<tr>
<td>Wu</td>
<td>0.937</td>
<td>Pyrolysis</td>
<td>0.789</td>
</tr>
<tr>
<td>Thomas</td>
<td>0.893</td>
<td>Activation</td>
<td>0.856</td>
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*Capacity: 10 mg, Step size: 1 s, Breakthrough: 3.3 mg, Dead volume: 0.2705 mg, Measurement time: 40 s, Time: 3/17/2010*
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