

An-Najah National University

Faculty of Engineering and

Information Technology



جامعة النجاح الوطنية
كلية الهندسة وتكنولوجيا المعلومات

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

Graduation Project Report 2

Removal of H₂S from biogas by activated carbon: Nablus Western Wastewater
Treatment Plant as a Case Study

By:

Dunia Ahmad Jazi -11716371

Reem Khalil Takrouri -11714999

Shaimaa Ra'fat Bani Mineh -11716897

Shaimaa Munther Hamadneh -11716557

Supervisor: Dr. Abdelrahim Abusafa

**Submitted in partial fulfillment of the requirements for Bachelor
Degree in Chemical Engineering**

Academic year 2021/2022

Table of contents

Abstract	iii
Chapter One Introduction	1
Constrains	3
Chapter Two Theoretical background	4
2.1 Factors affecting the adsorption process	4
2.2 Theoretical approach	6
2.3 Adsorption models studied.....	14
2.4 Summery	28
Chapter Three Methodology	31
Chapter Four Results and Discussion	34
4.1 Effect of biogas flow rate	34
4.2 Effect of H ₂ S concentration.....	36
4.3 Effect of the mass of activated carbon	37
4.4 Effect of Activated Carbon Bed Height	38
4.5 Comparing the experimental results with the theoretical results	40
4.6 How regeneration works	40
Chapter Five Conclusion and Recommendation.....	42
5.1 Conclusion.....	42
5.2 Recommendations	43
Chapter Six References.....	44

List of Figures

Figure 1-1: Production of biogas from different organic wastes	1
Figure 2.1-1: Effect of temperature on some adsorbents.....	4
Figure 2.2-1: Some common types of adsorption isotherms.	8
Figure 2.2-2: Concentration profile at various positions and times in the bed.....	11
Figure 2.2-3: Breakthrough concentration profile in the fluid at outlet of bed.....	11
Figure 2.2-4: Determination of capacity of column from breakthrough curve.....	13
Figure 3-1: Methodology flow chart.....	33
Figure 4.1-1: The effect of feed flowrate on the breakthrough curve utilizing AC with H ₂ S/ CH ₄ – CO ₂ feed.....	34
Figure 4.2-1: The effect of H ₂ S concentration on the breakthrough curve utilizing AC with H ₂ S/ CH ₄ – CO ₂ feed.....	36
Figure 4.3-1: The effect of mass of the activated carbon on the breakthrough curve.	37
Figure 4.4-1: Breakthrough curves for adsorption of H ₂ S onto AC for different bed height.	39

Abstract

Biogas, produced from anaerobic digestion of animal manure and waste water 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 absorption solvents to upgrade and purify biogas which is not economically feasible for small scale biogas systems. Activated carbon proves to be an effective adsorbent of hydrogen sulfide. Mathematical models for adsorption column such as Adam-Bohart and Thomas models were used. To predict the adsorption capacity, and breakthrough curves for this carbon material. The parameters like inlet H₂S concentration, flow rate, and mass of activated carbon were analyzed using Thomas model. However, the effect of bed height was investigated using Adam-Bohart model. The results showed that when the initial concentration was reduced, the adsorption efficiency increased; at the change of initial concentration from 1400 ppm to 400 ppm the breakthrough times were 21 and 76 days for initial concentration of 1400 and 400, respectively. It was also found that decreasing the flowrate of the treated gas, resulting in a shorter breakthrough time. The breakthrough time increased as the flow rate and initial H₂S concentration were reduced; the breakthrough time was 86 days when the flow rate was 0.0125 L/s and it was 36 days when the flowrate was 0.03 L/s. The results also show that the H₂S removal efficiency increased as the bed height increased.

In this study, based on the results, the best configuration of the bed height, flowrate, and adsorbent mass were 10 m, 0.0125 L/s, and 200 kg respectively. Two parallel columns will be utilized with adsorbent mass of 200 kg for each column, and the initial concentration of H₂S of 1400 ppm for each column. As a result of the high efficiency of adsorption at a low concentration, it is preferred to reduce this concentration to 400 ppm using other methods, such as biological treatment.

The regeneration of spent activated carbon was systematically studied by thermal regeneration method, and the number of times required for this method was calculated, which was once every three months. The annual used amount of activated carbon was 512 kg and its cost is \$194/year according to the required times for regeneration.

Chapter One

Introduction

Biogas is a promising renewable energy source that, in most developing nations, may be utilized to replace nonrenewable fossil fuels (e.g., Palestine and India). Biogas is often created through the anaerobic digestion of a variety of biomass feedstocks, such as animal, agricultural, and organic food waste. Methane, carbon dioxide, and percentages of water vapor and hydrogen sulfide (H_2S) make up the majority of the biogas produced, making H_2S a biogas impurity [1].

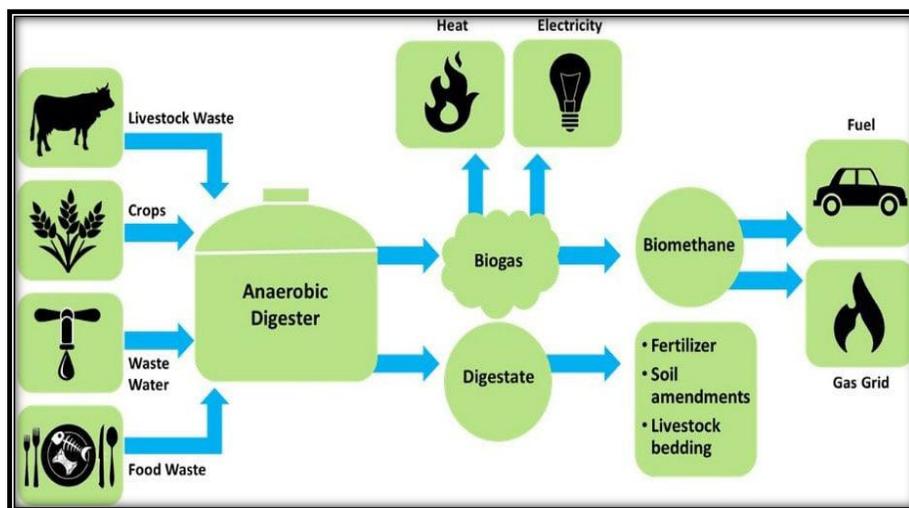


Figure 1-1: Production of biogas from different organic wastes [2].

The main component of biogas produced are methane (CH_4), along with a variety of additional impurities such as carbon dioxide (CO_2), nitrogen (N_2), oxygen (O_2), hydrogen (H_2), hydrogen sulfide (H_2S), ammonia (NH_3) and Siloxanes [3]. Biogas normally has a composition that falls between the following ranges, depending on the feedstock and digestion method: 50-70% methane (CH_4), 25-50% CO_2 , 1-5% H_2 , 0.3-3% N_2 and various minor impurities [4]. The presence of these impurities in biogas has a negative impact on engine performance and cause problems [5]. Of these problems, High concentration of O_2 is explosive, when biogas is utilized to generate energy, H_2S corrodes steel in reactors and engines and siloxanes can induce microcrystalline quartz to develop, which can deposit on surfaces and cause clogging problems [3]. Reducing of these impurities will significantly improve the quality of biogas [5]. Biogas with up to 45 % CO_2 content did not degrade

engine performance [6]. Thus, in this case, only other impurities are important to remove from it to improve the performance and avoid any cost-related problem. But in other cases, CO₂ and other impurities are completely removed to obtain biomethane [7]. For example, bio-methane can be used as a vehicle fuel to further reduce emissions compared to natural gas: for example, for carbon dioxide, the reduction will be about 90% [8].

In the literatures, various biological, chemical and physical techniques have been successfully studied for the purification of biogas from H₂S such as biological desulfurization, chemical absorption, water scrubbing, membranes and adsorption. Adsorption is one of the most effective technologies applied in removing H₂S from biogas streams. The high H₂S removal efficiency achieved by adsorption makes it superior over other purification techniques. Besides, it is a rather inexpensive technique with wide range of choices of low-cost adsorbents [1].

Objectives

The main objective of this project is to design a fixed-bed column theoretically using activated carbon to be used for biogas treatment in the western Nablus wastewater treatment plant. The objective of this project is divided into 2 sub-tasks:

1. Modeling hydrogen sulfide adsorption by activated carbon by studying six mathematical models and choosing the best models for design calculations.
2. Design a fixed bed adsorption column using activated carbon and optimize the design parameters based on the data available from the biodigester at Nablus western wastewater treatment plant.

Constrains

The process parameters such as column length, inlet biogas flow rate, initial hydrogen sulfide concentration of feed and characteristics of activated carbon for the packed bed adsorption column.

Based on some of the studies that have been reviewed such as (Anisuzzaman et al., 2016, [9]) and information that was benefited from the western Nablus wastewater treatment plant that one of the most factors affecting the breakthrough time is the column height and particular diameter , where the column height and particular diameter ranges 1-2 m and 0.45-1.5 mm , respectively .

An adsorption column will be designed as Aspen Plus simulation software was initially used, but some problems were encountered. So, mathematical models were used for adsorption columns by changing these parameters to obtain the best breakthrough curve.

Chapter Two

Theoretical background

2.1 Factors affecting the adsorption process

2.1A Temperature [10]

Fig. 2.1-1 shows that during adsorption processes, the adsorbed amount increases as the temperature decreases. Moreover, physisorption releases heat. So, as any exothermic reaction, it is favored by low temperatures.

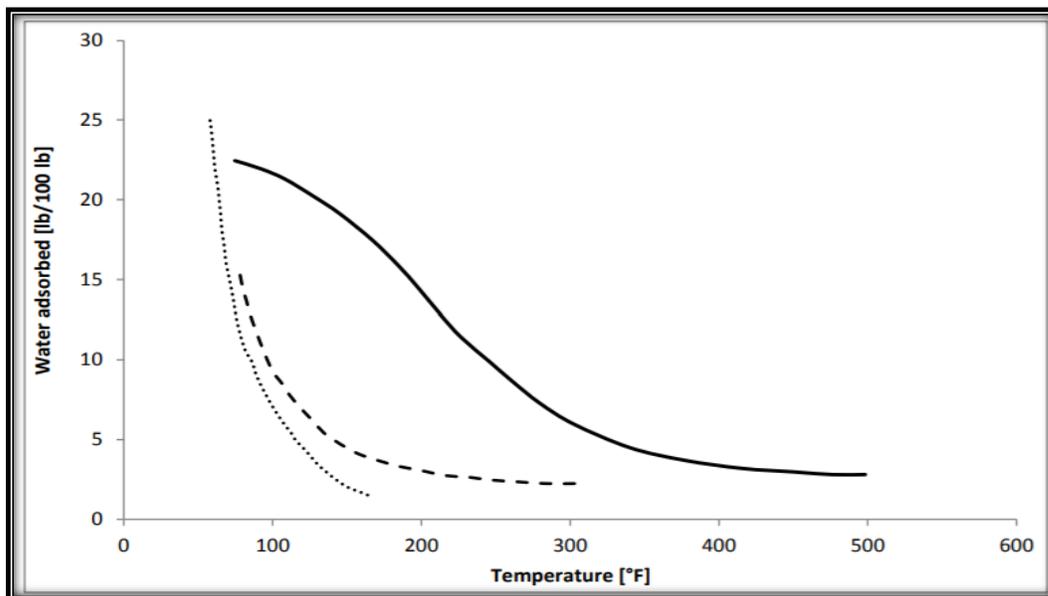


Figure 2.1-1: Effect of temperature on some adsorbents.

Unlike physical adsorption, chemical adsorption requires higher temperatures, because it is an endothermic phenomenon.

2.1B Humidity

A quick breakthrough was seen under dry conditions, and the outflow concentration grew rapidly as the processing time advanced. It can also be seen that with increased relative humidity, breakthrough time was delayed. Water, it can be argued, plays a critical part in the H₂S adsorption

process. When the humidity is high enough, a sufficient amount of water is absorbed, and water vapor is condensed capillary in the pores of activated carbons. As a result, a water film forms on the activated carbon's interior surface [11].

2.1C Specific surface area

Adsorption performance increases with the specific surface area of the adsorbent [10].

2.1D Selectivity

The concept of selectivity is crucial in the design of adsorption processes. The presence of competitive species at the surface of the adsorbent decreases the capacity of each species to be adsorbed. However, the higher the selectivity, the easier would be the separation [10].

2.1E Pore size distribution

Adsorption is a surface phenomenon, hence the interest of porous structures. The porosity of the adsorbent material is therefore an important physical property. For example, the microporous activated carbon has a better adsorption capacity than the mesoporous activated carbon in the case of macromolecules [10].

2.1F Molecular weight and structure

If the molecular weight of particles is low, it means that they are light and move faster than those with high molecular weight. The probability of being adsorbed is therefore much greater. If the molecular structure of particle is large, pores are filled rapidly with low yields to saturation, causing the decrease of free sites for other molecules [10].

2.1G Polarity

For more affinity between the adsorbent and the adsorbate, they must have the same polarity. For example, the structure of activated carbons is non-polar and therefore promotes the adsorption of nonpolar molecules. Hydrogen sulfide is a polar gas, it is adsorbed on the polar surfaces in the absence of water vapor. In the presence of water vapor in the gas, there is competitive adsorption to the advantage of water vapor which has a much higher partial pressure and which is much more polar than hydrogen sulfide [10].

2.1H Gas Composition

It was demonstrated that hydrogen sulfide can be oxidized on activated carbon under dry conditions in a nitrogen atmosphere. This demonstrates that the carbon material can oxidize sulfur compounds even when there is no oxygen present in the feed gas. The oxygen functional groups on the surface of the carbon material provide it its oxidation capacity. The presence of oxygen and carbon dioxide leads to slower kinetics than under pure nitrogen conditions [11].

2.2 Theoretical approach [12]

The mathematical model of the isothermal, dynamic adsorption breakthrough process in a fixed bed is based on transient material balance, gas phase and intra-fiber mass transfer, the adsorption equilibrium relationship, boundary conditions, and initial conditions. Two basic differential equations of the model are the mass balances for the adsorbate, both in the axial direction (x) and in the radial direction (r) of ACFs. The fluid phase mass balance describes the spatial and temporal variations of the adsorbate concentration in the main air-stream. The fiber column mass balance describes the removal rate of adsorbate from the gas phase into the adsorbent at a given axial location in the bed.

In fixed beds, the main parameters of transport of adsorbate are the axial dispersion coefficient and the fluid-to-ACFs mass transfer coefficient. The other important parameter, the intra-fiber diffusion coefficient is independent of the type of adsorption contactors.

The following are the mathematical descriptions derived from mass balances:

Air- stream phase

$$\frac{dc_a}{dt} = D_1 \frac{dc_a}{dx^2} - u \frac{dc_a}{dx} - \frac{2(1-\epsilon)}{R\epsilon} K_f (C_a - C_s) \quad (2.2-1)$$

Where:

C_a : is gas phase concentration (kg/m³).

t : is time(s).

D_i : is axial dispersion coefficient (m^2/s).

x : is axial distance from the adsorber bed entrance (m).

u : is interstitial velocity (m/s).

ε : is the porosity of ACFs adsorber bed.

K_f : is inter-phase mass transfer coefficient (m/s).

C_s : is the concentration at the surface of ACFs (kg/m^3).

2.2A ACF column

Adsorption in activated carbon is usually controlled by two diffusion processes. One is the diffusion of free species through the pore space, and the other is the surface migration of the adsorbed molecules. The surface diffusion could not be ignored in the adsorption of gases in activated carbon fiber, because its surface area is very large, of the order of $1000 m^2/g$. Therefore the equation for activated carbon fixed bed column (ACF) is:

$$(1 - \varepsilon_p) \frac{dq_i}{dt} + \varepsilon_p \frac{dC_{ai}}{dt} = \varepsilon_p D_{ei} \left(\frac{d^2 C_{ai}}{dr^2} + \frac{1}{r} \frac{dC_{ai}}{dr} \right) + (1 - \varepsilon_p) D_{si} \left(\frac{d^2 q_i}{dr^2} + \frac{1}{r} \frac{dq_i}{dr} \right) \quad (2.2-2)$$

Where:

ε_p : is the porosity of ACF bed.

q_i : is adsorbed phase concentration (kg/m^3).

C_{ai} : is intra-fiber gas phase concentration (kg/m^3).

D_{ei} : is an effective gas-phase diffusion coefficient in tortuous pores (m^2/s).

r : is the radial distance from the center of ACF (m).

D_{si} : is surface diffusion coefficient (m^2/s).

2.2B Equilibrium Relations for Adsorbents [13]

The equilibrium between the concentration of a solute in the fluid phase and its concentration on the solid resembles somewhat the equilibrium solubility of a gas in a liquid. Data are plotted as adsorption isotherms as shown in Fig. 2.2-1. The concentration in the solid phase is expressed as q , kg adsorbate/kg adsorbent (solid), and in the fluid phase (gas or liquid) as c , kg adsorbate/m³ fluid.

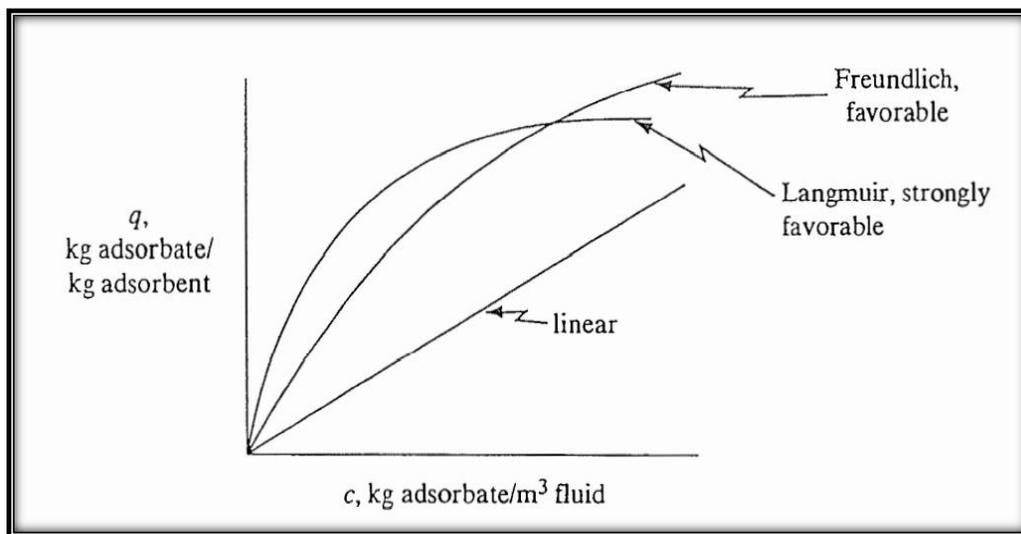


Figure 2.2-1: Some common types of adsorption isotherms.

Data that follow a linear law can be expressed by an equation similar to Henry's law ($P = KHC$).

$$q = Kc \quad (2.2-3)$$

Where:

K : is a constant experimentally, m³/kg adsorbent.

The Freundlich isotherm equation, which is empirical, often approximates data for many physical adsorption systems and is particularly useful for liquids.

$$q = Kc^n \quad (2.2-4)$$

Where:

K and n are constants and experimentally. a log-log plot of q versus c is made, the slope is the dimensionless exponent n. The dimensions of K depend on the value of n. This equation is sometimes used to correlate data for hydrocarbon gases on activated carbon.

The Langmuir isotherm has a theoretical basis and is given by the following, where q_0 , and K are empirical constants.

$$q = \frac{q_0 c}{K + c} \quad (2.2-5)$$

Where:

q_0 : is a constant, kg adsorbate/kg solid.

K: is a constant, kg/m^3 .

Initial conditions [12]

The initial conditions are

$$C_a = C_{a0} \quad \text{for } x \geq 0 \text{ and } t = 0$$

$$q_i = q_{i0} \quad \text{for } r \geq 0 \text{ and } t = 0$$

$$C_{ai} = C_{ai0} \quad \text{for } r \geq 0 \text{ and } t = 0$$

Where:

C_{a0} : is initial gas concentration in fluid (kg/m^3)

q_{i0} : is initial adsorbed phase concentration (kg/m^3)

C_{ai0} : is the initial gas-phase concentration (kg/m^3).

Boundary conditions [12]

The boundary conditions are:

$$D_1 \frac{dC_a}{dx} = -u(C_{in} - C_a) \text{ for } x = 0 \text{ and } t > 0$$

Where C_{in} is gas phase inlet concentration (kg/m^3).

$$\frac{dC_a}{dx} = 0 \text{ for } x = L \text{ and } t > 0$$

$$\frac{dq_i}{dr} = 0 \text{ for } r = 0 \text{ and } t > 0$$

$$\frac{dC_{ai}}{dr} = 0 \text{ for } r = 0 \text{ and } t > 0$$

2.2C Breakthrough curve [13]

As seen in Fig. 2.2-2, the major part of the adsorption at any time takes place in a relatively narrow adsorption or mass-transfer zone. As the solution continues to flow, this mass-transfer zone, which is S-shaped, moves down the column. At a given time t_3 in Fig. 2.2-2 when almost half of the bed is saturated with solute, the outlet concentration is still approximately zero, where H is the bed height.

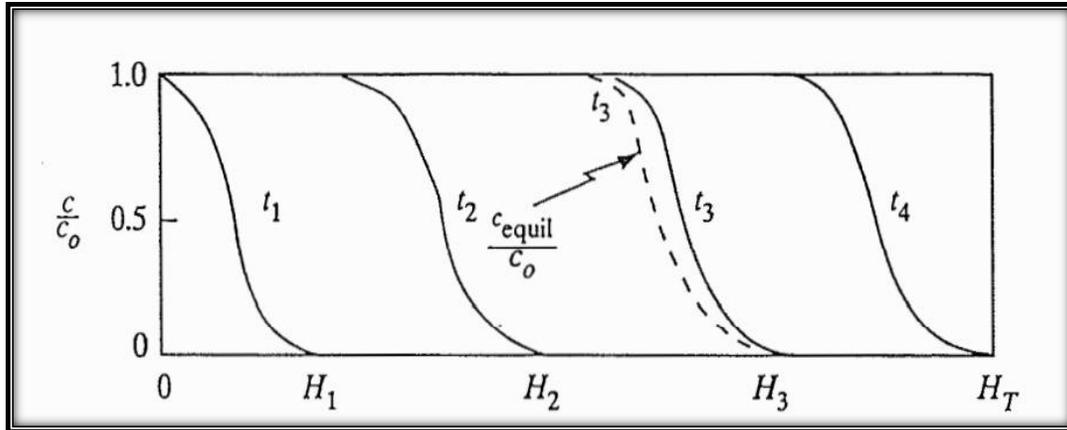


Figure 2.2-2: Concentration profile at various positions and times in the bed.

as shown in Fig. 2.2-3. This outlet concentration remains near zero until the mass-transfer zone starts to reach the tower outlet at time t_4 . Then the outlet concentration starts to rise and at t_5 is the outlet concentration has risen to c_b , which is called the break point. After the break-point time is reached, the concentration c rises very rapidly up to point c_d , which is the end of the breakthrough curve where the bed is judged ineffective. The break-point concentration represents the maximum that can be discarded and is often taken as 0.01 to 0.05 for c_b/c_0 . The value c_d/c_0 is taken as the point where c_d is approximately equal to c_0 .

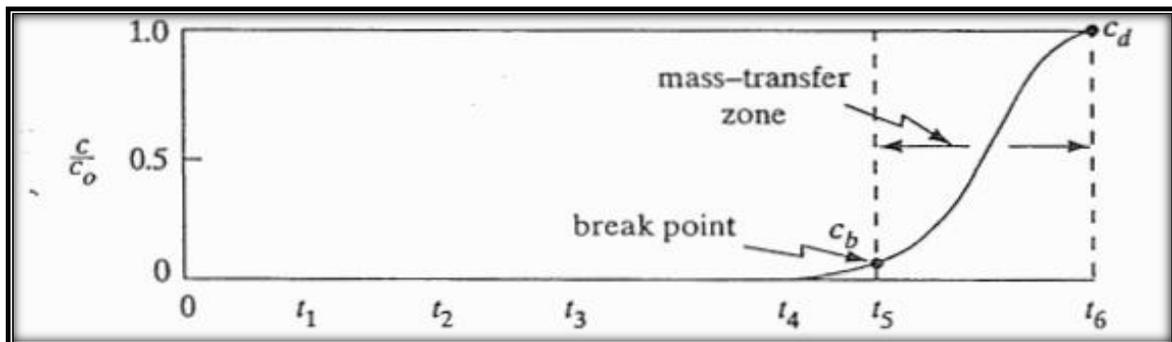


Figure 2.2-3: Breakthrough concentration profile in the fluid at outlet of bed.

For a narrow mass-transfer zone, the breakthrough curve is very steep and most of the bed capacity is used at the break point. This makes efficient use of the adsorbent costs for regeneration.

2.2D Capacity of column and scale up design method

The mass-transfer zone width and shape depend on the adsorption isotherm, flow rate, mass-transfer rate to the particles, and diffusion in the pores. A number of theoretical methods have been published which predict the mass-transfer zone and concentration profiles in the bed. The predicted results may be inaccurate because of many uncertainties due to flow patterns and correlations to predict diffusion and mass transfer. Hence, experiments in laboratory scale are needed in order to scale up the results.

The total or stoichiometric capacity of the packed - bed tower, if the entire bed comes to equilibrium with the feed, can be shown to be proportional to the area between the curve and a line at $c/c_0 = 1.0$ as shown in Fig. 2.2-4. The total shaded area represents the total or stoichiometric capacity of the bed as follows:

$$t_t = \int_0^{\infty} \left(1 - \frac{c}{c_0}\right) dt \quad (2.2-6)$$

Where:

t_t : is the time equivalent to the total or stoichiometric capacity.

The usable capacity of the bed up to the break – point time t_b is the crosshatched area as follow:

$$t_u = \int_0^{t_b} \left(1 - \frac{c}{c_0}\right) dt \quad (2.2-7)$$

Where:

t_u : is the time equivalent to the usable capacity or the time at which the effluent concentration reaches its maximum permissible level. The value of t_u is usually very close to that of t_b .

The ratio t_u/t_t is the fraction of the total bed capacity or length utilized up to the break point. Hence, for a total bed length of H_T m, H_B is the length of bed used up to the break point,

$$H_B = \frac{t_u}{t_t} \times H_T \quad (2.2-8)$$

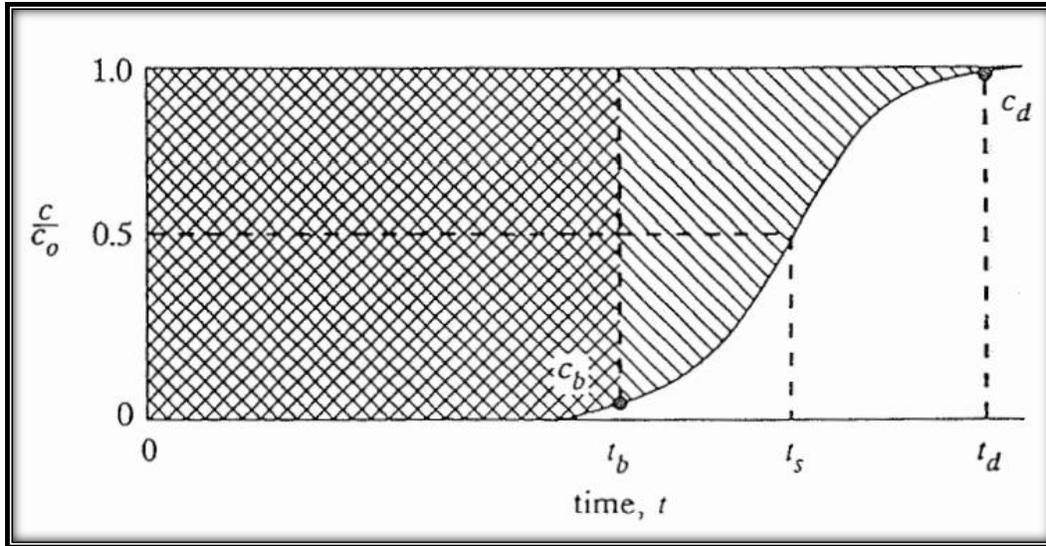


Figure 2.2-4: Determination of capacity of column from breakthrough curve.

The length of unused bed H_{UNB} in m is then the unused fraction times the total length.

$$H_{UNB} = \left(1 - \frac{t_u}{t_t}\right) H_T \quad (2.2-9)$$

The H_{UNB} represents the mass-transfer section or zone. It depends on the fluid velocity and is essentially independent of total length of the column. The value of H_{UNB} may, therefore, be measured at the design velocity in a small-diameter laboratory column packed with the desired adsorbent. Then the full-scale adsorber bed can be designed simply by first calculating the length of bed needed to achieve the required usable capacity, H_B , at the break point. The value of H_B is directly proportional to t_b . Then the length H_{UNB} of the mass-transfer section is simply added to the length H_B needed to obtain the total length, H_T .

$$H_T = H_{UNB} + H_B \quad (2.2-10)$$

This design procedure is widely used and its validity depends on the conditions in the laboratory column being similar to those for the full - scale unit. The small - diameter unit must be well insulated to be similar to the large - diameter tower, which operates adiabatically. The mass velocity in both units must be the same and the bed of sufficient length to contain a steady - state

mass transfer zone. Axial dispersion or axial mixing may not be exactly the same in both towers, but if caution is exercised this method is a useful design method.

An approximate alternative procedure to use instead of integrating and obtaining areas is to assume that the breakthrough curve in Fig. 2.2-4 is symmetrical at $c/c_0 = 0.5$ and t_s . Then the value of t_t in Eq. (2.2-6) is simply t_s . This assumes that the area below the curve between t_b and t_s is equal to the area above the curve between t_s and t_d .

2.2E Adsorption capacity [14]

The adsorption capacity of activated carbon was measured using the breakthrough time, flow rate, and length of bed used, as shown in the following equation:

$$Q = \frac{q \times T_B \times C \times MW_{H_2S}}{V_M \times m_{ads}} \quad (2.2-11)$$

Where:

Q: (mg H₂S/g) refers to adsorption capacity.

q: (L/min) is feed flow rate.

T_B: (min) is breakthrough time.

C: (kg/L) is breakthrough concentration.

MW_{H₂S}: (kg/kmol) is the molecular weight of H₂S.

V_M: (L) is molar volume at S.T.P.

m_{ads}: (kg) is mass adsorbent used.

2.3 Adsorption models studied [15]

The sections to follow explore six different adsorption models which were studied. 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.

2.3A Adam and Bohart Model

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.

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

$$\frac{\partial C}{\partial t} + v \frac{\partial C}{\partial x} + \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial q}{\partial t} = 0 \quad (2.3-1)$$

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.

ε : is bed porosity (dimensionless).

q: is the adsorbate concentration in the adsorbent (g adsorbate/L adsorbent).

Kinetics of adsorption are described using the quasichemical rate law below:

$$\frac{\partial q}{\partial t} = kC(q_e - q) \quad (2.3-2)$$

Where:

q_e : is the constant value of q that corresponds to the equilibrium condition at the gas/adsorbent interface (g adsorbent/L carbon).

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.

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

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

$$\frac{C}{C_0} = \frac{\exp(\tau)}{\exp(\tau) + \exp(z) + 1} \quad (2.3-3)$$

Where:

$$\tau = kC_0\left(t - \frac{x}{u}\right) \quad (2.3-4)$$

And

$$z = \frac{kq_s x}{u\left(\frac{1-\varepsilon}{\varepsilon}\right)} \quad (2.3-5)$$

Where:

q_s : is the adsorptive capacity of the adsorbent (g/L).

2.3B Thomas Model

Thomas developed a model that uses Langmuir isotherm for equilibrium, and 2nd order reversible reaction kinetics based on ion exchange theory.

The continuity equation of the column is written as,

$$v \frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} + \frac{\rho}{\varepsilon} \frac{\partial q}{\partial t} = 0 \quad (2.3-6)$$

Where:

v: 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).

ρ : is bulk density of the carbon (g/dm³).

ε : is porosity of the bed (dimensionless).

The expression for adsorption kinetics is described as,

$$\frac{\partial q}{\partial t} = K_1(q_0 - q)C - k_2q(C_0 - C) \quad (2.3-7)$$

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).

C_0 : is the inlet concentration of adsorbate in the gas stream (g adsorbate/L).

The above expression describes 2nd 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.

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,

$$\frac{c}{c_0} = \frac{1}{1 + \exp\left[\frac{K_T(q_0 m_c - c_0 V_{eff})}{Q}\right]} \quad (2.3-8)$$

Where:

K_T : is the Thomas rate constant ($\text{dm}^3/(\text{s} \cdot \text{g})$).

q_0 : is the adsorptive capacity of the carbon (g/g).

m_c : is the mass of carbon in the column (g).

V_{eff} : is the throughput volume (L).

Q : is the volumetric flow rate (dm^3/s).

2.3C Yoon and Nelson Model

Theoretical model developed by Yoon and Nelson 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,

$$-\frac{dQ}{dt} \propto QP \quad (2.3-9)$$

Where:

Q (%): is the probability for adsorption.

P (%): is the probability for breakthrough.

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). Therefore,

$$-\frac{dQ}{dt} \propto \frac{CU}{W_c} QP \quad (2.3-10)$$

By introducing a dimensionless constant of proportionality, k, we have

$$-\frac{dQ}{dt} = \frac{kCU}{W_c} QP \quad (2.3-11)$$

Or,

$$-\frac{dQ}{dt} = K_{YN} QP \quad (2.3-12)$$

Where:

$$K_{YN} = CU/W_c .$$

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

$$\ln \frac{C_0}{C_0 - C} = K_{YN}t - t_{0.5}K_{YN} \quad (2.3-13)$$

Where:

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

2.3D Clark Model

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:

$$J = \frac{v_s A C - v_s A (C - \Delta C)}{A \Delta Z} \quad (2.3-14)$$

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).

C: is the influent adsorbate concentration into the differential element volume (g/L).

Z: is the reactor height (dm).

Simplifying and taking the limit below:

$$\lim_{\Delta Z \rightarrow \infty} \frac{\Delta C}{\Delta Z} = \frac{dC}{dZ} \quad (2.3-15)$$

Then equation 2.3-14 can be simplified to the equation below:

$$J = v_s \frac{dC}{dZ} \quad (2.3-16)$$

The following mass transfer coefficient concept is used,

$$K_T(C - C_e) = v_s \frac{dC}{dZ} \quad (2.3-17)$$

Or rearranged to:

$$\frac{dC}{C - C_e} = \frac{K_T dZ}{v_s} \quad (2.3-18)$$

Where:

K_T : is the mass transfer coefficient in (s^{-1}).

C_e : is the equilibrium value of adsorbate at the gas/carbon interface (g adsorbate/dm³ carbon).

With the assumption that all gas is removed at the end of the column, the ideal mass balance over the entire column is:

$$v_s C = L_a q \quad (2.3-19)$$

Or rearranged to:

$$\frac{C}{q} = \frac{L_a}{v_s} \quad (2.3-20)$$

Where:

L_a : is the mass velocity of adsorbent to keep the mass transfer zone stationary (g carbon/s*dm²).

q : is the concentration of adsorbate per unit weight of adsorbent (g adsorbate/g carbon).

Using the Freundlich isotherm between the adsorbent and gas yields:

$$X = K(C_e)^{\frac{1}{n}} \quad (2.3-21)$$

Or,

$$C_e = \left(\frac{1}{K}\right)^n X^n \quad (2.3-22)$$

Where:

K: is the equilibrium constant and 1/n is the slope of the isotherm.

Substituting equations 2.3-20 and 2.3-22 into 2.3-18 yields equation 2.3-23 below:

$$\frac{dC}{C - \left[\left(\frac{1}{K}\right)^n \left(\frac{v_s}{L_a}\right)^n\right] C^n} = \left(\frac{K_T}{v_s}\right) dZ \quad (2.3-23)$$

Using the boundary condition below:

At $t = t_b$ (breakthrough time).

$C = C_b$ (concentration at breakthrough time) equation 2.3-23 was solved by Clark and the solution below was found where $n \neq 1$.

$$\frac{C}{C_0} = \left(\frac{1}{1 + Ae^{-rt}}\right)^{\frac{1}{n-1}} \quad (2.3-24)$$

Where:

$$A = \left(\frac{C_0^{n-1}}{C_b^{n-1}} - 1\right) e^{rt_b} \quad (2.3-25)$$

$$r = R(n - 1) = \frac{K_T}{v_s} v_m (n - 1) \quad (2.3-26)$$

Where:

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

$$V = \frac{uC_0}{N_0 + C_0} \quad (2.3-27)$$

Where:

U: is the gas flow rate (L/s).

N_0 : is the adsorptive capacity of the carbon (g adsorbate/L carbon).

2.3E Wolborska Model

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

1. A low concentration region in the range from 10^{-5} to 5×10^{-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.

- 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.

Below is the continuity equation on the column:

$$\frac{\delta C}{\delta t} + u \frac{\delta C}{\delta h} + \frac{\delta q}{\delta t} = D \frac{\delta^2 C}{\delta h^2} \quad (2.3-28)$$

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 2.3-28 becomes:

$$(u - w) \frac{dc}{dx} - w \frac{dq}{dx} = D \frac{d^2c}{dx^2} \quad (2.3-29)$$

and the initial and boundary conditions are $c(x,0) = 0$, $q(x,0) = 0$, $c(0, \tau) = c_0$, 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,

$$\frac{\delta q}{\delta t} = \beta(c - c_i) \quad (2.3-30)$$

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, $c_i \ll c$.

Then:

$$-w \frac{dq}{dx} = \beta_0 c \quad (2.3-31)$$

Where $\beta_0 = \beta$ when $t \rightarrow 0$.

Inserting expression 2.3-29 into equation 2.3-31, the following differential equation is obtained.

$$\frac{d^2c}{dx^2} - \frac{(u-w)}{D} \frac{dc}{dx} - \frac{\beta_0 c}{D} = 0 \quad (2.3-32)$$

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

$$\ln \frac{c}{c_0} = \frac{\beta_a c_0}{q_0} t - \frac{\beta_a}{u} h \quad (2.3-33)$$

Where for process without axial diffusion

$$\beta_a = \beta_0 \quad (2.3-34)$$

and for column dynamics with axial dispersion.

$$\beta_a = \frac{u^2}{2D} \left(\sqrt{1 + \frac{4\beta_0 D}{u^2}} - 1 \right) \quad (2.3-35)$$

2.3F Zhang and Cheng Model

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

$$\frac{\partial \emptyset}{\partial t} = K_d \emptyset \quad (2.3-36)$$

Where:

t: is time (s).

\emptyset : is the deactivation function (dimensionless).

K_d (s^{-1}): is the deactivation rate constant.

Given the initial condition, when $t = 0$, then $\phi = 1$, and taking the derivative of 2.3-36, equation 2.3-37 is obtained for the deactivation function. The solution below is true for separable deactivation kinetics resulting from contact with a catalyst poison at a constant concentration (inlet concentration) and no spatial variation.

$$\phi = e^{-K_d t} \quad (2.3-37)$$

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

$$R = KC\phi = KCe^{-K_d t} \quad (2.3-38)$$

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:

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + \frac{1-\epsilon}{\epsilon} \rho \frac{\partial q}{\partial t} + R = 0 \quad (2.3-39)$$

Where:

u: is superficial velocity (dm/s).

x: is the distance from the bed inlet (dm).

ϵ : is bed porosity (dimensionless).

q: is the adsorbate concentration in the carbon (g adsorbate/g carbon).

ρ : is the bulk density of the carbon (g/dm³).

The physical adsorption is characterized by a linear isotherm as at small concentrations, the Langmuir isotherm is linear.

$$q = K_i C \quad (2.3-40)$$

Then taking the derivative of equation 2.3-40 with respect to time, the following expression is obtained,

$$\frac{\partial q}{\partial t} = K_i \frac{\partial C}{\partial t} \quad (2.3-41)$$

Where:

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

The above partial differential equation 2.3-39 was solved by Zhang et al. Using the stream line method and the boundary conditions below.

- At $x = 0, t > 0, C = C_o$
- At $t = 0, x > 0, C = 0$

The following solution is given below:

$$\ln \ln \frac{C_o}{C} = \ln \frac{K}{[1 + \frac{K_i \rho (1 - \epsilon)}{\epsilon}] K_d} - K_d t + \ln \left\{ e^{\frac{K_d x [1 + \frac{K_i \rho (1 - \epsilon)}{\epsilon}]}{u}} - 1 \right\} \quad (2.3-42)$$

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

$$\ln \ln \frac{C_o}{C} = a - K_d t \quad (2.3-43)$$

Where:

$$a = \ln \frac{K}{\alpha K_d} + \ln \left(e^{\frac{K_d \alpha L}{u}} - 1 \right) \quad (2.3-44)$$

$$\alpha = 1 + \frac{K_i \rho (1 - \varepsilon)}{\varepsilon} \quad (2.3-45)$$

Where:

L: is the length of the bed (dm).

2.3G Activated carbon cost [16]

Carbon Cost, C_c , in dollars (\$) is simply the product of the initial carbon requirement (Mc) and the current price of carbon (CC).

$$C_c = CC \times Mc \quad (2.3-46)$$

2.4 Summary

From the models studied above, the best models were obtained for the design of the adsorption bed are Adam and Bohart model and the Thomas model. For Thomas model, it will be used to predict the mass of adsorbent required, inlet concentration of H₂S, and the flow rate of biogas. As for Adam and Bohart model, it will be used to predict the bed height required.

Table 1: Describes the comparison between the mathematical models.

Model name	Adam-Bohart	Thomas	Yoon and Nelson
Differential equation	$\frac{\partial C}{\partial t} + v \frac{\partial C}{\partial x} + \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial q}{\partial t} = 0$ $\frac{\partial q}{\partial t} = kC(q_e - q)$	$v \frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} + \frac{\rho}{\varepsilon} \frac{\partial q}{\partial t} = 0$ $\frac{\partial q}{\partial t} = K_1(q_o - q)C - k_2q(C_0 - C)$	$-\frac{dQ}{dt} = \frac{kCU}{Wc} QP$ $-\frac{dQ}{dt} = K_{YN}QP$

Final equation	$\frac{C}{C_0} = \frac{\exp(\tau)}{\exp(\tau) + \exp(z) + 1}$ $\tau = kC_0\left(t - \frac{x}{u}\right)$ $z = \frac{kq_s x}{u\left(\frac{1-\varepsilon}{\varepsilon}\right)}$	$\frac{C}{C_0} = \frac{1}{1 + \exp\left[\frac{K_T(q_0 m_c - C_0 V_{eff})}{Q}\right]}$	$\ln \frac{C}{C_0 - C} = K_{YN}t - t_{0.5}K_{YN}$
Assumptions	negligible axial dispersion	By assuming plug flow, negligible axial dispersion	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
Usage	For estimate the concentration of H ₂ S in the effluent Flowrate	For estimate the concentration of H ₂ S in the effluent Flowrate	For estimate the concentration of H ₂ S in the effluent Flowrate

Model name	Clark	Wolborska	Zhang and Cheng
Differential equation	$J = \frac{v_s A C - v_s A (C - \Delta C)}{A \Delta Z}$	$\frac{\delta C}{\delta t} + u \frac{\delta C}{\delta h} + \frac{\delta q}{\delta t} = D \frac{\delta^2 C}{\delta h^2}$ $(u - w) \frac{dC}{dx} - w \frac{dq}{dx} = D \frac{d^2 C}{dx^2}$	$\frac{\partial \phi}{\partial t} = K_d \phi$ $\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} + \frac{1-\varepsilon}{\varepsilon} \rho \frac{\partial q}{\partial t} + R = 0$
Final equation	$\frac{C}{C_0} = \left(\frac{1}{1 + A e^{-rt}}\right)^{\frac{1}{(n-1)}}$ $A = \left(\frac{C_0^{n-1}}{C_b^{n-1}} - 1\right) e^{rt_b}$ $r = R(n - 1) = \frac{K_T}{v_s} v_m (n - 1)$	$\ln \frac{C}{C_0} = \frac{\beta_a C_0}{q_0} t - \frac{\beta_a}{u} h$ $\beta_a = \beta_0$ $\beta_a = \frac{u^2}{2D} \left(\sqrt{1 + \frac{4\beta_0 D}{u^2}} - 1 \right)$	$\ln \ln \frac{C_0}{C} = a - K_d t$ $a = \ln \frac{K}{\alpha K_d} + \ln \left(e^{\frac{K_d \alpha L}{u}} - 1 \right)$ $\alpha = 1 + \frac{K_i \rho (1 - \varepsilon)}{\varepsilon}$

Assumptions	all gas is removed at the end of the column	low concentration	the bed dynamics follow ideal plug flow with no axial dispersion, and isothermal conditions, then the superficial gas velocity is kept constant
Usage	For estimate the concentration of H ₂ S in the effluent Flowrate	For estimate the concentration of H ₂ S in the effluent Flowrate	For estimate the concentration of H ₂ S in the effluent Flowrate

Chapter Three

Methodology

In this study, a packed bed adsorption column will be designed theoretically using Thomas and Adam-Bohart models to reduce the concentration of H₂S from 1400 ppm to 50 ppm in biogas with a flowrate of approximately 2200 Nm³/day at the wastewater treatment [17].

Packed-bed systems are widely used in the adsorption of water vapor, organic solvent, and some toxic gases. A simple packed bed system consists of a single column loaded with a particular type of adsorbent. In a single packed-bed system, the appropriate type of adsorbent is chosen for each adsorbate to achieve high removal efficiency [18].

Reaching the breakthrough curve is the basis of the adsorption column design. So, will be studying the influence of parameters like inlet H₂S concentration, flow rate, mass of adsorbent, and bed height on the breakthrough curve to reach the optimum design.

The methodology that will be used in this study is given as follows:

Step 1: Study and understand all the six models (Adam-Bohart, Thomas, Yoon and Nelson, Clark, Wolborska, and Zhang and Cheng) then choose the best models (Thomas and Adam-Bohart models) that achieve the desired goal for this project, collect all the data related to them and search for how to calculate the constant parameters of each model.

Step 2: In the Thomas model, the hydrogen sulfide concentration and flow rate are fixed, while the adsorbent mass changes. By several trying, more than one value for the adsorbent mass is substituted in the Thomas model as shown in **Eq. 2.3-8** and plot this relation by Excel.

Step 3: By applying the same model in step 2, the adsorbent mass and the flow rate are fixed while the H₂S concentration changes. By several trying, more than one value for the H₂S concentration is substituted in the **Eq. 2.3-8**.

Step 4: By applying the same model in step 2, the adsorbent mass and the H₂S concentration are fixed while the flowrate changes. By several trying, more than one value for the flowrate is substituted in the **Eq. 2.3-8**.

Step 5: Then the Adam- Bohart model is applied to study the effect of the height of the absorption column on the breakthrough curve by fixing the column diameter, H₂S concentration and flow rate. By several trying, more than one value for the column height is substituted in the Adam-Bohart model as shown in **Eq. 2.3-3** and plot this relation by Excel.

Step 6: Choose a bed height, H₂S concentration, adsorbent mass, and flow rate that provide reasonable breakthrough time, pressure drop and cost (optimum design).

Step 7: Calculate the cost of activated carbon and the annual amount used in the adsorption process.

This methodology is explained in the Flow chart as shown in Fig. 3-1:

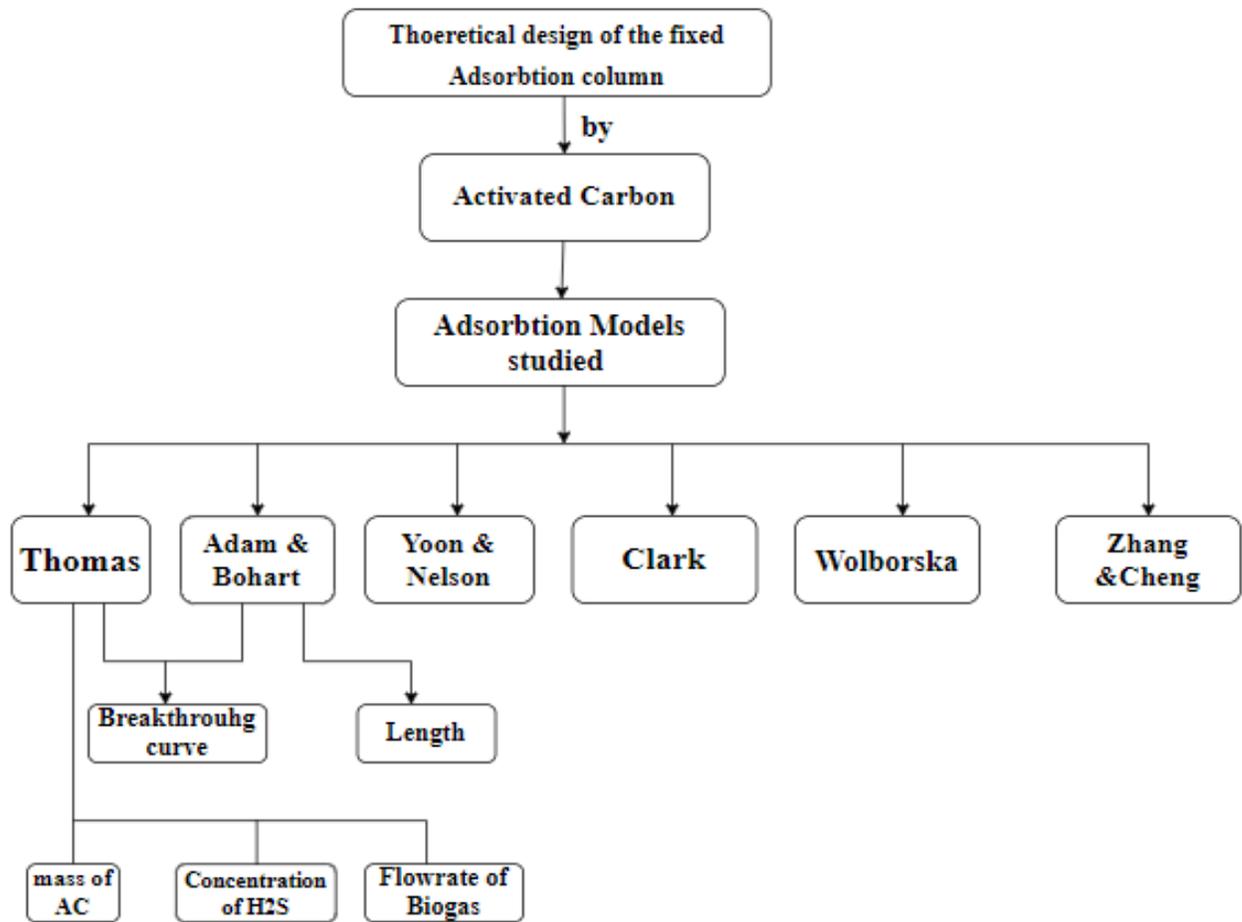


Figure 3-1: Methodology flow chart.

Chapter Four

Results and Discussion

Optimizing the adsorption bed size is based on the following parameters: Gas flow rate, concentration and mass of activated carbon in Thomas model. While the length of the adsorption column and diameter in Adam and Bohart model. The temperature for the operation is at 25°C and the pressure is at atmospheric condition. The diameter of the adsorbent layer was set at 0.5 m while the height of the adsorbent layer varies. It found the height which has a breakthrough time of over one month to be 10 m.

In this project, a comparison between experimental results for H₂S adsorption (from literature) with the Bohart–Adams (B–A) model and the Thomas model was made.

4.1 Effect of biogas flow rate

By keeping other parameters constant, varying the flow rates of biogas, show significant differences in results between the various flow rates. Fig. 4.1-1 shows the breakthrough of hydrogen sulfide at various flow rates.

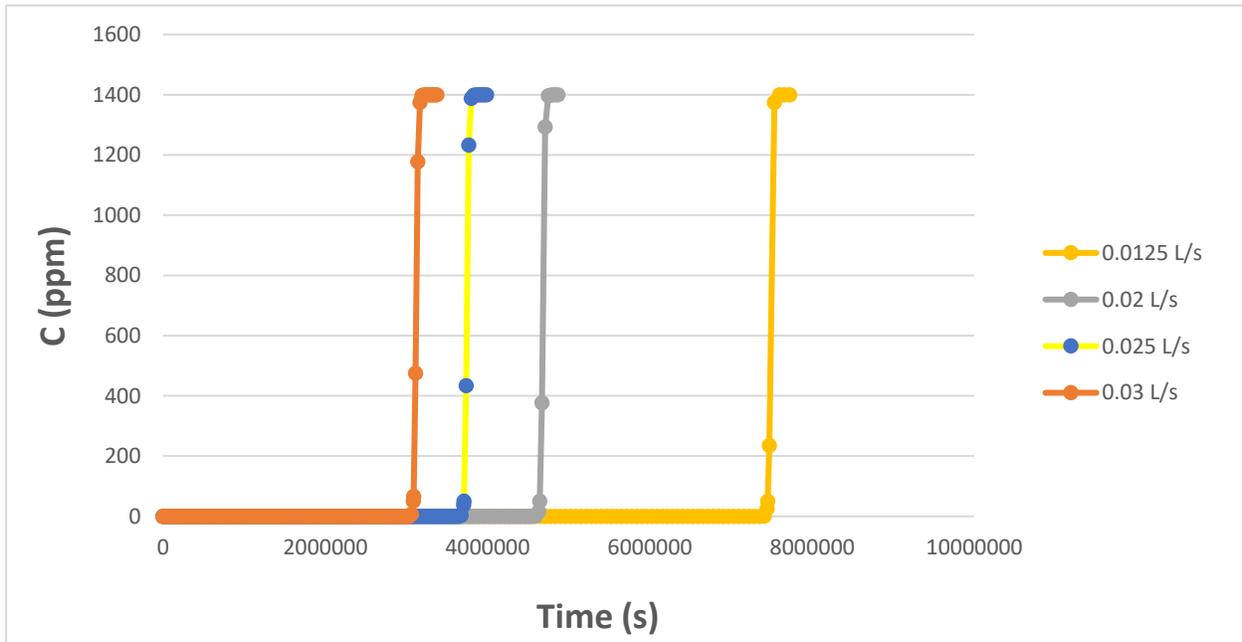


Figure 4.1-1: The effect of feed flowrate on the breakthrough curve utilizing AC with H₂S/ CH₄ – CO₂ feed.

The flow rates 0.0125, 0.02, 0.025 and 0.03 were used in the Thomas model while the concentration was kept constant at 1400 ppm. The large difference in flow rates shows that the breakthrough time is long at low flow rate. This happens because at low flow rate, the adsorption of H₂S onto the active site of the adsorbent is less. Which will not block the active sites rapidly. However, at high flow rates of the treated gas at a higher speed at which the adsorption of H₂S to the active site of the AC rapidly increases. Resulting in blockage of active sites of AC at a faster rate. The estimated breakthrough time from the graph for the different flow rates 0.0125, 0.02, 0.025 and 0.03 L/s were 86, 54, 43 and 36 days, respectively. The flowrate of 0.0125 L/s was required a very long time to reach the breakthrough point. This is because the flow provides enough H₂S for adsorption. From Fig. 4.1-1 the H₂S capacity at the breakthrough point of the flowrates of 0.0125, 0.02, 0.025 and 0.03 L/s were 0.887, 0.884, 0.882 and 0.88 mg/g respectively. But, the maximum H₂S capacity was 1.67 mg/g.

Fig. 4.1-1 it shows that a lower flow rate takes longer to reach the breakout point. This indicates that the flow rate (0.025 L/sec) provided by the Western Wastewater Treatment Plant in Nablus may not occur in a short time. This is because the breakthrough time is too short. Which leads to the regeneration of activated carbon in a short time in the adsorption column. Thus, increasing the number of activated carbon regeneration times. So, in this study, two adsorption columns will be used in parallel for treating the flowrate of 0.025 L/s. This means, that in each column, the inlet flow rate is 0.0125 L/s. Furthermore, this leads to an increase in breakthrough time. Thus, reducing the number of regeneration times and its cost.

4.2 Effect of H₂S concentration

To retrieve the result of the breakthrough curve by varying the concentration of H₂S. The flow rate of the biogas was kept constant. From Fig. 4.2-1, the lower concentration takes longer to reach the concentration ratio (C/C_0) of 1.

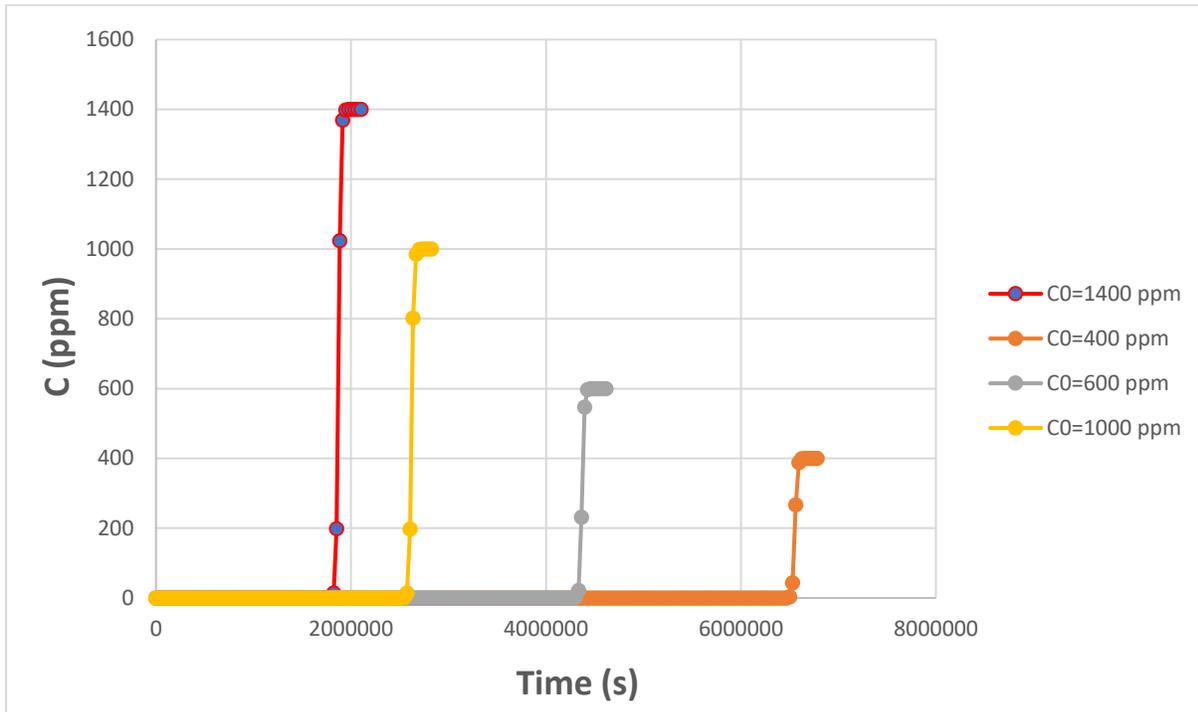


Figure 4.2-1: The effect of H₂S concentration on the breakthrough curve utilizing AC with H₂S/ CH₄ – CO₂ feed.

The concentrations 400, 600, 1000, and 1400 ppm were used in the Thomas model, while the flow rate was kept constant at 0.025 L/s.

For example, when the concentration is 400 ppm, the mass-transfer zone represented the area between the curve and a line at $C/C_0 = 1$ as shown in Fig. 4.2-1. Which reaches the end of the bed at the breakthrough time. The outlet concentration would rapidly rise over the maximum permissible outlet (or "breakthrough") concentration until it approached the inlet concentration. Thus, some adsorbate leaves with the column effluent, which usually is not desirable. This is called breakthrough, and the time 76 days is referred to as the breakthrough time when the concentration is 400 ppm, and 50 days at concentration of 600 ppm, and 30 days at concentration of 1000 ppm

and 21 days at concentration of 1400 ppm. From Fig. 4.2-1, the adsorption is more effective at low concentrations but the concentration in the biogas flow rate in this study is 1400 ppm. It is preferable to reduce it by other feasible methods.

4.3 Effect of the mass of activated carbon

The flow rate of the biogas and the concentration of H₂S had to be kept constant in order to recover the result of the breakthrough curve by varying the quantity of activated carbon. The large mass of AC takes longer time to reach the concentration ratio (C/C₀) of 1, as seen in Fig. 4.3-1.

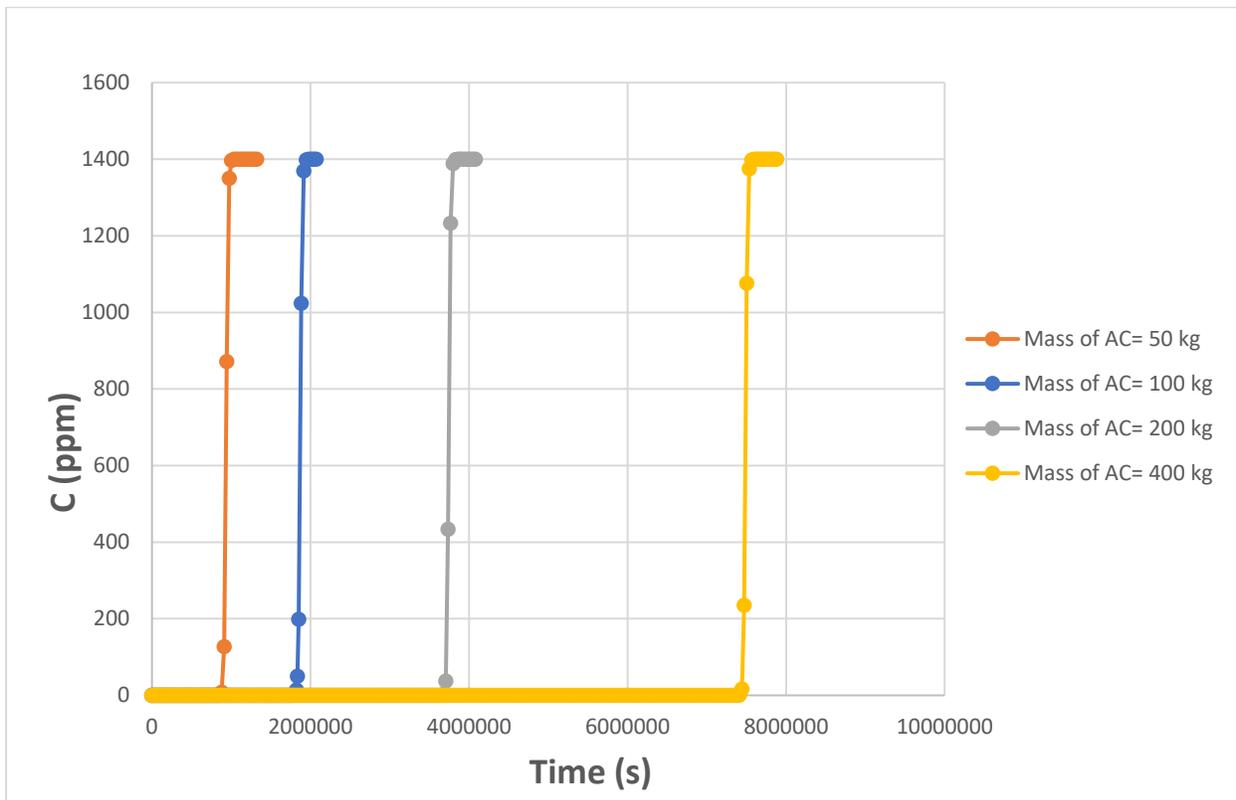


Figure 4.3-1: The effect of mass of the activated carbon on the breakthrough curve.

The masses of activated carbon 50, 100, 200 and 400 Kg were used in the Thomas model. While, the flow rate and concentration of H₂S were kept constant at 0.025 L/s and 1400 ppm, respectively. The activated carbon has excellent adsorption characteristics due to its high specific surface area and the presence of small pores of various sizes. Thus, the increase of adsorbent mass would

provide a larger service area leading to an increase in the volume of the treated biogas. From the Fig. 4.3-1, the H₂S capacities at the breakthrough point of the flowrates of 0.025 were 0.857, 0.874, 0.883, and 0.887 mg/g for the masses of 50, 100, 200, and 400 Kg, respectively. While the maximum H₂S capacity was 1.67 mg/g.

In addition, the H₂S adsorption capacity could be affected by stream conditions, such as the moisture content. According to the literature [16], the moisture content has no effect on the functional capacity of activated carbon if the inflow concentration is greater than 1,000 ppm. When the H₂S inlet concentration is less than 1,000 ppm or the relative humidity is greater than 50%, the moisture competes with the adsorbate for available adsorption sites. Dehumidification equipment can be utilized to lower the moisture content of the biogas stream before it enters the adsorber column if the H₂S concentration is below 1,000 ppm or the relative humidity is above 50%.

In this project, the inlet concentration which was supplied from the Nablus western wastewater treatment plant is 1400 ppm and it's greater than 1000 ppm. So, the moisture content in the biogas stream does not affect the absorption capacity of H₂S.

4.4 Effect of Activated Carbon Bed Height

Fig. 4.4-1 shows the breakthrough curve obtained for adsorption of H₂S on AC at constant adsorbate feed flow rate of 0.025 L/s and adsorbate inlet concentration of 1400 ppm. Since two adsorption columns will be used in parallel as explained in the section 4.1, the flow rate in each column will be 0.0125 L/s. The bed heights 2, 6, 8 and 10 are used in the Adam and Bohart model. Model parameters of most importance are bed height L, initial concentration C₀, volumetric flow rate Q, and bed diameter D. It was found that if the flow rate and the bed height decreased, the breakthrough time decreased. A longer bed contains more adsorbent, which allows longer online time before adsorbent regeneration is needed as shown in Fig. 4.4-1.

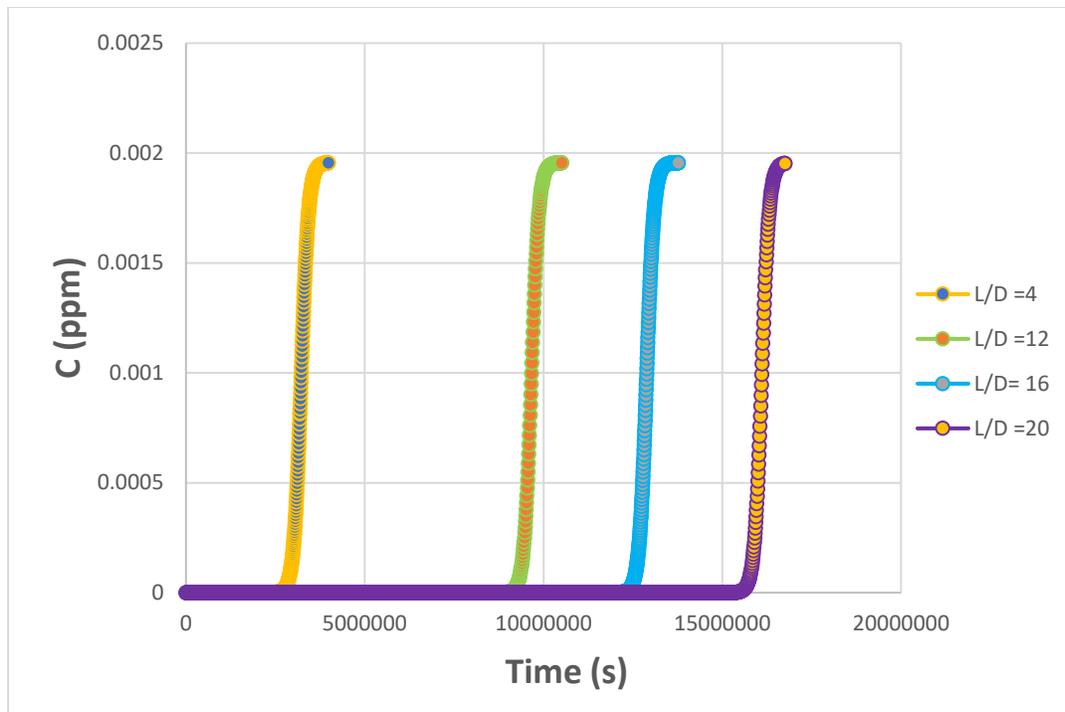


Figure 4.4-1: Breakthrough curves for adsorption of H₂S onto AC for different bed height.

As shown by the curves (Fig. 4.4-1), the breakthrough time increased with increasing bed height. The curves represent that the shape of the breakthrough curves differed from the bed height variation. Also, higher adsorption is achieved by the higher bed height. It is because of the increased amount of activated carbon. The increase in bed height will increase the mass transfer zone. The mass transfer zone in a column moves from the entrance of the bed and proceeds towards the exit. Furthermore, an increase in bed height would create a longer distance for the mass transfer zone to reach the exit. Resulting in an extended breakthrough time.

On the downside, if the column is too tall, then two absorbent columns should be used in series with recompressing steps to prevent the pressure drop.

4.5 Comparing the experimental results with the theoretical results

According to the literature [19], the experimental and predicted breakthrough curves for the adsorbent LG700PA at four inlet concentrations of H₂S (162, 570, 1065 and 1980 ppm). Where the rest of operating parameters were kept constant. When comparing with solving the models, it becomes clear that there is no significant difference between the experimental results and the theoretical results. As it was found that when the concentration increases, the time decreases in both results. Whereas, the best time for the literature was at a concentration of 162 ppm and the best time in this study was at a concentration of 400 ppm.

4.6 How regeneration works [20]

The most frequent method of regeneration is thermal, in which high temperatures are utilized to remove the adsorbed components. While the process varies depending on the source material and adsorbed components, there are three steps in general.

First, the material is dried. Volatilization can occur after the material has been dried to the required moisture level. When the material is heated to roughly 1000°F, 75–90% of the adsorbed materials volatilize. Steam is fed into the system at this point to eliminate any leftover volatiles and to "reactivate" the carbon.

The result is near-completely restored activated carbon ready for reuse. During this process, it is common to have carbon losses between 5 – 10%. As a result, when spent carbon is regenerated, that amount of new activated carbon must be added to compensate for the losses. These stages may be completed in one piece of equipment or in numerous parts, depending on a variety of conditions. The activated carbon is frequently cooled in a rotary cooler after regeneration before being shipped, stored, or reused.

4.6A Cost of the activated carbon based on the regeneration times

Amount of activated carbon that used 400 kg for two columns. Regeneration time every 3 month (Four time in the year) based on the optimum results. Each time a regeneration process is made, 5-10% of the new activated carbon will be used, and assumed 7% is used:

Then $0.07 * 400 * 4 = 112$ kg of AC added /year

Then the total AC needed is 512 kg in the year

The cost of AC \$0.38/kg [21], then the total cost of AC according to the **Eq. 2.3-46** is:

$$512 * 0.38 = \$194 \text{ /year}$$

Chapter Five

Conclusion and Recommendation

5.1 Conclusion

An adsorption column is designed to remove some impurities such as H₂S and reduce its concentration from 1400 to 50 ppm. The results showed that granular activated Carbon (GAC) is an effective and low-cost adsorbent for the removal of H₂S from biogas. The process variables such as flow rate, bed height, adsorbent mass, and initial H₂S concentration have a significant impact on the adsorption of H₂S in a fixed bed column. Within the studied flowrates of 0.0125, 0.02, 0.025, and 0.03 L/s an optimum breakthrough point was found at a flow rate of 0.0125 L /s for a breakthrough concentration of 50 ppm. The fixed bed adsorption system was found to perform better with lower H₂S inlet concentration, lower feed flow rate, higher adsorbent mass, and higher GAC bed height.

The case study plant produces a 2200 Nm³/day (25 L/s), which is a very high flowrate, the project calculations were performed based on Thomas and Adam-Bohart models. This high flowrate was not suitable to be applied using this type of models. As a results, a recommended flowrate (low flowrate) has been utilized in order to get a correct result.

In the conclusion of this study:

- The best configuration of the bed height, flowrate, and adsorbent mass were 10 m, 0.0125 L/s, and 200 kg, respectively.
- Two parallel columns will be utilized with adsorbent mass of 200 kg for each column.
- The annual used amount of activated carbon was 512 kg and its cost is \$194/year according to the required times for regeneration.

5.2 Recommendations

- It is possible Using software programs such as Aspen Plus Simulation.
- It is possible to use a higher column diameter and study its effect.
- It is possible to study two parameters at the same time but in ways other than modeling.
- It is possible to study other properties of adsorption such as adsorption efficiency.

Chapter Six

References

- [1] H. Sawalha, M. Maghalseh, J. Qutaina, K. Junaidi, and E. R. Rene, "Removal of hydrogen sulfide from biogas using activated carbon synthesized from different locally available biomass wastes - a case study from Palestine," *Bioengineered*, vol. 11, no. 1, pp. 607–618, Jan. 2020, doi: 10.1080/21655979.2020.1768736.
- [2] "Fact Sheet | Biogas: Converting Waste to Energy | White Papers | EESI." <https://www.eesi.org/papers/view/fact-sheet-biogasconverting-waste-to-energy> (accessed Dec. 19, 2021).
- [3] "Biogas Cleaning and Upgrading Technologies | Ohioline." <https://ohioline.osu.edu/factsheet/AEX-653.1-14> (accessed Dec. 19, 2021).
- [4] S. Bari, "Effect of carbon dioxide on the performance of biogas/diesel dual-fuel engine," *Renewable Energy*, vol. 9, no. 1–4, pp. 1007–1010, Sep. 1996, doi: 10.1016/0960-1481(96)88450-3.
- [5] N. Tippayawong and P. Thanompongchart, "Biogas quality upgrade by simultaneous removal of CO₂ and H₂S in a packed column reactor," *Energy*, vol. 35, no. 12, pp. 4531–4535, Dec. 2010, doi: 10.1016/J.ENERGY.2010.04.014.
- [6] S. A. Ahmad *et al.*, "Effects of CO₂ ratio in Biogas on Performance, Combustion and Emissions of a Dual-Fuel Diesel Engine," *International Energy Journal*, pp. 15–38, 2020.
- [7] Associazione Italiana Di Ingegneria Chimica., *ICheaP11- Special ISSUE 11th International Conference on Chemical and Process Engineering: 2-5 June 2013, Milan, Italy*. Associazione italiana di ingegneria chimica, 2013.
- [8] "The benefits and the usage." https://www.snam.it/en/energy_transition/biomethane/benefits_and_usage/ (accessed Dec. 19, 2021).
- [9] S. M. Anisuzzaman, A. Bono, D. Krishnaiah, and Y. Z. Tan, "A study on dynamic simulation of phenol adsorption in activated carbon packed bed column," *Journal of King*

- Saud University - Engineering Sciences*, vol. 28, no. 1, pp. 47–55, Jan. 2016, doi: 10.1016/J.JKSUES.2014.01.001.
- [10] H. Cherif, “Study and modeling of separation methods H₂S from methane, selection of a method favoring H₂S valorization.” [Online]. Available: <https://pastel.archives-ouvertes.fr/tel-01764942>
- [11] N. Ho, “Modeling Hydrogen Sulfide Adsorption by Activated Carbon made from Anaerobic Digestion By-Product,” 2012.
- [12] T. Cheng, Y. Jiang, Y. Zhang, and S. Liu, “Prediction of breakthrough curves for adsorption on activated carbon fibers in a fixed bed,” *Carbon N Y*, vol. 42, no. 15, pp. 3081–3085, 2004, doi: 10.1016/j.carbon.2004.07.021.
- [13] C. J. Geankoplis, *Transport Processes and Unit Operations*, Third. The United States of America.
- [14] N. N. Zulkefli, M. S. Masdar, W. N. Roslam Wan Isahak, J. M. Jahim, S. A. Md Rejab, and C. C. Lye, “Removal of hydrogen sulfide from a biogas mimic by using impregnated activated carbon adsorbent,” *PLOS ONE*, vol. 14, no. 2, p. e0211713, Feb. 2019, doi: 10.1371/JOURNAL.PONE.0211713.
- [15] N. Ho, “Modeling Hydrogen Sulfide Adsorption by Activated Carbon made from Anaerobic Digestion By-Product,” 2012.
- [16] J. L. Sorrels, A. Baynham, D. D. Randall, and K. S. Schaffner, “Chapter 1 - Carbon Adsorbers,” 2018.
- [17] “محطات معالجة مياه الصرف الصحي – 11/2021 تقرير اعمال محطة التنقية الشهري” <http://wwtp.nablus.org/?p=3677> (accessed May 21, 2022).
- [18] S. M. Anisuzzaman, A. Bono, D. Krishnaiah, and Y. Z. Tan, “A study on dynamic simulation of phenol adsorption in activated carbon packed bed column,” *Journal of King Saud University - Engineering Sciences*, vol. 28, no. 1, pp. 47–55, Jan. 2016, doi: 10.1016/j.jksues.2014.01.001.

- [19] P. G. Aguilera and F. J. Gutiérrez Ortiz, “Prediction of fixed-bed breakthrough curves for H₂S adsorption from biogas: Importance of axial dispersion for design,” *Chemical Engineering Journal*, vol. 289, pp. 93–98, Apr. 2016, doi: 10.1016/j.cej.2015.12.075.
- [20] “Activated Carbon Thermal Regeneration – Activated Carbon.” <https://www.acarbons.com/activated-carbon-thermal-regeneration/>? (Accessed Dec. 19, 2021).
- [21] “Activated Carbon - Activated Charcoal Latest Price, Manufacturers & Suppliers.” <https://dir.indiamart.com/impcat/activated-carbon.html> (accessed May 22, 2022).