



Removal of H₂S Biogas Using Synthesized Activated Carbon from Different Biomass Waste

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Submitted to the College of Engineering

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Dedication

*We would like to dedicate this work to
our beloved Parents and families
For their love, endless support, encouragement
and sacrifices*

&

to the

*Environmental engineering staff and students, who has
given us wisdom & knowledge,
patience, and love.*

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ABSTRACT

This project aims at the removal of H₂S from biogas by adsorption using synthesized activated carbon. The effect of type of precursors, activation reagent and packed bed height were studied. Adsorption test was performed using a fixed bed filter filled with the produced activated carbon where the inlet biogas has H₂S concentration of 930-970 ppm. The AC was synthesized according to a previous study H.Sawalha, A.Bader, J.Sarsour, "Preparation of Activated Carbon through Pyrolysis of Agricultural Waste for Wastewater Treatment Applications". Three types of biomasses: almond shells, eucalyptus and coffee grains were collected, grinded, sieved, pyrolysed at 500°C and activated with chemical reagents KOH or ZnCl₂. Two centimeter of each precursors activated with KOH were used in precursor's effect study. H₂S outlet concentration decreased to less than 10 ppm for all samples. The best performance was for eucalyptus followed by almond shells and coffee grains. The outlet H₂S concentration reached the inlet concentration in 182, 130, 9 minutes respectively. As for activation chemical, KOH has higher efficiency than ZnCl₂ in which 2 cm of eucalyptus activated with KOH consumed 182 minutes while with ZnCl₂ consumed 70 minutes only. In bed height effect study, 2, 4, 6 and 8 cm of coffee grains were used. Removal efficiency increased with amount of AC in which the outlet H₂S concentration reaches the inlet concentration within 12, 42, 90 and 170 minutes respectively.

The main conclusion of the present study is that synthesized activated carbon could be successfully applied for removal of H₂S from the biogas.

Key words: Adsorption, H₂S removal, activated carbon, pyrolysis, activation, fixed bed.

المخلص

يهدف هذا المشروع لفصل غاز كبريتيد الهيدروجين H_2S من الغاز الحيوي وذلك باستخدام الفحم المنشط و الذي تم إنتاجه خلال عملية الانحلال الحراري والتنشيط الكيميائي للنفايات النباتية. وتم خلال البحث دراسة تأثير ثلاث عوامل على عملية فصل غاز H_2S عن الغاز الحيوي وهي نوع النفايات العضوية المستخدمة و نوع المادة الكيميائية المستخدمة في التنشيط إضافة إلى كمية الفحم النشط المستخدم. تمت عملية الامصاص باستخدام غاز حيوي يحتوي ٩٣٠-٩٧٠ جزء في المليون من غاز H_2S . وتم تصنيع الفحم المنشط بناء على دراسة سابقة للباحثين د. صوالحة، م. بدر، م. صرصور. حيث تم تجميع ثلاث أنواع من هذه النفايات وهي قشور اللوز، الكينيا و القهوة و طحنها و تخيلها. ومن ثم تمت عملية الانحلال الحراري على درجة حرارة ٥٠٠ °م وبعد ذلك التنشيط الكيميائي باستخدام هيدروكسيد البوتاسيوم (KOH) أو كلوريد الزنك ($ZnCl_2$) كمواد كيميائية لعملية التنشيط . وتم اختبار عملية ادمصاص كبريتيد الهيدروجين بالفحم المنشط. بعد دراسة تأثير نوع النفايات العضوية انخفض تركيز غاز H_2S إلى أقل من ١٠ أجزاء في المليون عند استخدام ٢ سم من العينات الثلاث المنشطة باستخدام KOH. وقد كانت أعلى كفاءة للكينيا ثم اللوز وبعد ذلك القهوة، بحيث أن الوقت اللازم لتركيز H_2S الخارج من الفلتر حتى يصل إلى التركيز الداخل كان ١٨٢ دقيقة للكينيا، ١٣٠ للوز و ٩ دقائق للقهوة. أما بالنسبة للمادة الكيميائية المستخدمة في التنشيط فقد لوحظ أن فعالية هيدروكسيد البوتاسيوم أعلى من فعالية ملح كلوريد الزنك، حيث أن ٢سم من الكينيا المنشطة باستخدام KOH احتاجت ما يقارب ١٨٠ دقيقة كي يتساوى التركيز الداخل بالتركيز الخارج، بينما باستخدام $ZnCl_2$ احتاجت ٧٠ دقيقة. أما عند دراسة كمية الفحم المستخدم تم استخدام ٢، ٤، ٦ و ٨ سم من القهوة المنشطة باستخدام KOH ولوحظ أن الكفاءة تزداد بازدياد كمية الفحم النشط المستخدم. حيث أن الوقت المستغرق ليتساوى التركيز الداخل بالخارج كان ١٢ دقيقة ل ٢ سم، ٤٢ دقيقة ل ٤ سم، ٩٠ دقيقة ل ٦ سم، و ١٧٠ دقيقة ل ٨ سم.

الخلاصة الرئيسية من هذا البحث هي أن الفحم المنشط المصنوع من النفايات النباتية يمكن أن يستخدم بشكل فعال لتنقية الغاز الحيوي من غاز كبريتيد الهيدروجين.

Chapter One

Research concept

1.1 Introduction

Biomass waste is being produced in large amounts and it can be utilized to produce biogas through anaerobic digestion. The produced biogas can be used to generate energy by releasing heat from combustion reaction. Various types of gasses are produced during fermentation in addition to methane CH_4 including carbon dioxide CO_2 , hydrogen sulfide H_2S , and moisture H_2O . These pollutants adversely affect electricity generation process.

Sources used to produce biogas including household waste, wastewater treatment plant sludge, agricultural waste, landfill, and the waste of agrifood industry. The compositions of biogas differ according to the source of production, which depend on the substrate, organic matter load and the feeding rate to the digester. Table 1.1 shows the variation in biogas composition depending on the type of waste.

Table 1.1 Composition of biogas from different sources [1].

Component	Household waste	wastewater treatment plant sludge	agricultural waste
CH_4 vol%	50 - 60	60 – 75	60 – 75
CO_2 vol%	34 - 38	19 – 33	19 – 33
N_2 vol%	0 - 5	0 -1	0 -1
O_2 vol%	0 -1	< 0.5	< 0.5
H_2O vol%	6	6	6
H_2S mg /m ³	100 - 900	1000 – 4000	3000-10000

The range of H_2S concentration in biogas was reported by several researchers between 0-5 % v/v. This ratio depends on the type of waste used in biogas generation which differ in water content, pH and sulfur content. However, the presence of hydrogen sulfide in biogas is not desirable due to many reasons; its toxicity, bad odor and because it's lethal for human in a

concentration larger than 1000 ppm within a few seconds [2]. Dissolved hydrogen sulfide with concentration upwards 50 mg/L causes fermentation inhibition because it is toxic to the bacteria in the slurry [2]. H₂S is also corrosive for metallic parts used in biogas plant facilities. Furthermore, H₂S oxidized during combustion to form acidic sulfur dioxide (SO₂) which is a very high corrosive gas. Based on these reasons, it was necessary to search for technology to purify biogas from H₂S; several methods are used for desulfurization of biogas as follows:

1. Biological desulfurization by addition of air

Hydrogen sulfide can be oxidized into elemental sulfur by microorganisms that grow on the surfaces when adding 8 to 12% by volume fresh air. Sulfur accumulates on the surfaces and ultimately passes back into the substrate, where it is partly converted into H₂S again. The efficiency of this process is limited and methane content of biogas is significantly reduced [2].

2. Chemical absorption

A substance such as a liquid or gas is involved the formation of reversible chemical bonds between solute and solvent. The most chemicals used are solutions of alkaline salts. Expensive investment requires heat for regeneration, corrosion, decomposition, and poisoning of amines by O₂ or other chemicals and precipitation of salts are common disadvantages for chemical absorption [3].

3. Water scrubbing

In this method absorption process operated when water is fed on the top of backed bed and biogas is fed from the bottom. This method can be used for selective removal of H₂S since H₂S is more soluble than CO₂ in water. This method is undesirable since it requires a large amount of water, causes corrosion to the equipment by H₂S and has a limitation on H₂S removal due to excess of CO₂[4].

4. Membranes

A membrane is a layer of material with fine pores, which is selective between two substances when it's exposed to driving force. High-pressure separation process and selectivity separate H_2S and CO_2 from CH_4 . The permeability of gasses through membrane depends on their solubility in the membrane material. Membranes have low selectivity and expensive. Comparing between purity of CH_4 and the amount of upgraded biogas, multiple steps required to reach high purity so CH_4 is lost [4].

5. Adsorption

A process in which molecules (gas or liquid) adhere to a surface of a solid by attraction forces in physical adsorption or by chemical reactions in chemical adsorption. The most used adsorbents for gasses are silica gel, zeolites, synthetic resins, and activated carbon, as shown in Figure 1.1.

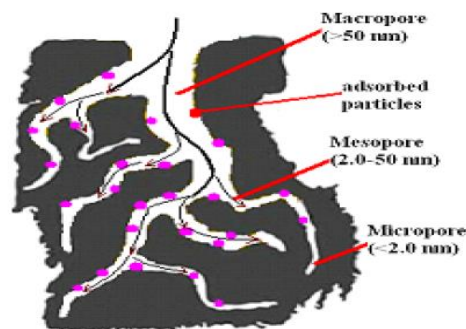


Figure 1.1 Pores inside activated carbon[5].

Activated carbon (AC) is widely available, relatively inexpensive, and highly efficient due to the high surface area, adsorption capacity, and surface reactivity. AC is used in many applications such as petroleum refining, wastewater treatment, air pollution treatment and volatile organic compounds (VOC) adsorption [6], and gold purification [7]. AC can be obtained through pyrolysis of different substances including rubber, tires, coal, petroleum pitch, and biomass.

Several types of biomasses were utilized in the literature for the production of AC such as nutshells, coconut husk, peat and wood. Lignocellulosic biomass can be categorized into three different components, mainly cellulose, hemicellulose, and lignin, which is responsible for the adsorption process in AC [6]. AC is usually classified by its size and shape into powdered, granulated, spherical, or pelleted activated carbons. It can be activated by physical or chemical activation. AC was mostly applied for wastewater treatment. However, only few studies reported in applications of AC in gas purification.

1.2 Problem Statement

This research study deals with the following main and sub main problems:

❖ **Research main problem:**

What is the technical feasibility of using synthesized AC from biomass in a packed bed to be applied for H₂S removal from biogas?

❖ **Sub problems:**

1. What is the effect of the type of biomass on H₂S removal efficiency and time needed for AC to be saturated?
2. How does the chemical activation reagent e.g KOH and ZnCl₂ affect H₂S removal efficiency and time needed for AC to be saturated?
3. What is the effect of bed height on H₂S removal efficiency and time needed for AC to be saturated?

1.3 Goals and Objectives

The objective of this study is to prepare AC from various types of biomass waste for application in biogas purification i.e. H₂S removal.

The main objectives are:

- ✓ To prepare AC using various low-cost biomass wastes including almond shells, eucalyptus barks and coffee grains.
- ✓ To purify biogas from H₂S using adsorbents prepared through pyrolysis of biomass wastes.
- ✓ To study the effects of bed height on adsorption conditions in the adsorption process.
- ✓ To study the effects of activation chemical in the activation process.

1.4 Significance of Study

This project tends to remove H₂S from biogas for environmental and safety measures as it is a toxic and has bad odor. As well as to provide high efficiency production of electricity, protect equipment in the facility from corrosion by H₂S and provide a cheap technology for biogas purification by treating waste by waste.

1.5 Methodology

The AC from biomass wastes produced through pyrolysis and then activated through chemical activation. Biogas purification implemented by continuous adsorption using a bed of synthesized AC.

1.6 Budget

This project is estimated to have a total cost of 400 \$ as Table 1.2 lists

Table 1.2 Total estimated cost for implementing this project

NO	Item	Cost \$
1	Crushing & grinding	20
2	Chemicals for activation	20
3	Lab tools (beakers, crucibles, tubes...)	100
4	Packed bed for activated carbon	10
5	Pipes and connection tools	50
6	H ₂ S sensor	220
7	Muffle furnace	9000
8	Other indirect costs	200
	Total	9620\$

1.7 Action Plan

The First Semester

TASKS	1 st Month				2 nd Month				3 rd Month				4 th Month			
	W ₁	W ₂	W ₃	W ₄	W ₁	W ₂	W ₃	W ₄	W ₁	W ₂	W ₃	W ₄	W ₁	W ₂	W ₃	W ₄
Identification of Project Idea																
Literature Review																
Collecting Biomass																
Activation of biomass																
Carbonization of Biomass																
Adsorption Tests																
Documentation																
Presentation																

The Second Semester

TASKS	1 st Month				2 nd Month				3 rd Month				4 th Month			
	W ₁	W ₂	W ₃	W ₄	W ₁	W ₂	W ₃	W ₄	W ₁	W ₂	W ₃	W ₄	W ₁	W ₂	W ₃	W ₄
Preparation of Samples																
Carbonization of Biomass																
Activation of Carbon																
Adsorption Test																
Documentation																
Final Presentation																

Chapter Two

Literature Review

Activated Carbon Production

2.1 Introduction

A lot of agricultural and industrial activities produce large amounts of biomass residues and wastes which cause an environmental problem. These wastes can be converted to a valuable products i.e. activated carbon. Production of AC from wastes not only solves environmental problem but also achieves economic gains. AC production is based on carbonizing and activating either physically or chemically.

2.2 Carbonization

Biomass can be used to generate energy through heat conversion in three main processes, pyrolysis, gasification, and combustion. Pyrolysis is a thermal decomposition of biomass in a medium does not contain oxygen that produces different energy forms such as char, bio-oil and fuel gas [8]. Gasification is the production of a gaseous fuel from biomass through heating in a gaseous medium such as air, nitrogen, carbon dioxide, oxygen, or steam. The produced gas that consists of CO, CO₂, H₂, and N₂ can be used as a chemical feedstock to produce liquid fuels. On the other hand, it can be used in power gas engines and gas turbines to generate electricity or in boilers for heat generation [9]. As for combustion, it is the direct burning of biomass in the presence of oxygen which converts the chemical energy stored in biomass to heat within a temperature range of 800– 1000 °C [8]. Combustion ensures the complete oxidation of the biomass while gasification is a partial oxidation in temperature ranges between 700-900 °C. Figure 2.1 summarize the heat conversion processes of biomass and their products.

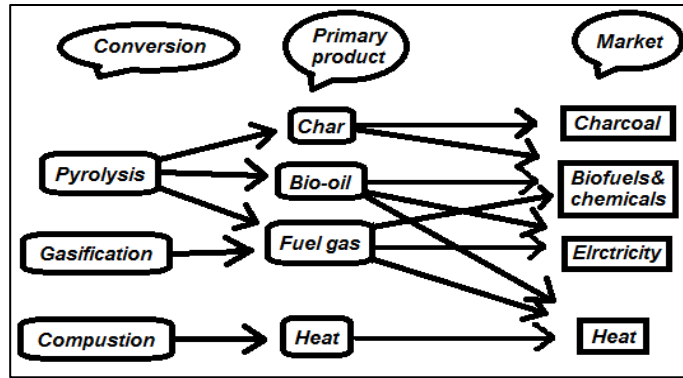


Figure 2.1 Heat conversion processes of biomass and their products [10].

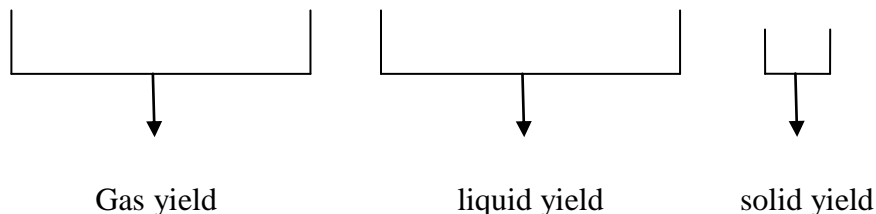
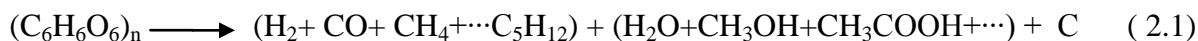
This study is interested in the production of AC from biomass, which is called biochar, so the study focuses on pyrolysis.

2.1.1 Pyrolysis

It is thermo-chemical decomposition in the absence of oxygen. Pyrolysis can be applied in organic waste, which has a high content of hemicelluloses, cellulose, and lignin; these components can be decomposed by the effect of high temperature. The absence of oxygen allows the temperature to increase above the biomass thermal stability temperature, which produces more stable products without burning.

Different chemical reactions take place during pyrolysis; these reactions can be divided into two stages: primary and secondary. In the primary stage when biomass is heated to a temperature around 200 °C the carbohydrate polymers partially depolymerize to short chains of sugar units. This process is accompanied with a slow dehydration to give species with low content of water. When the temperature reaches 300°C, a series of interactions occur involving devolatilization, removal of volatile material, and dehydrogenation, removal of hydrogen from organic molecules. The result of this step is the formation of different carbonyl groups, carbon atom double-bonded to an oxygen atom: C=O, hydroxyl groups, entity with the formula OH, and carboxyl groups, carbonyl, and hydroxyl group both linked to a carbon

atom. In the secondary stage at higher temperatures, the heavy compounds start cracking and C-C bond breaking down to give char or gasses, and sometimes the resulted gasses condense to give bio-oil.[8,11,12] Equation 2.1 shows the formula of different yields from pyrolysis [8].



2.1.2 Types of pyrolysis

The type of pyrolysis depends on temperature, residence time, and heating rate. It can be categorized as shown in Table 2.1.

Table 2.1 Operating conditions for different types of pyrolysis [8].

Process	Slow	Fast	Flash	Intermediate
Temperature(°C)	550-950	850-1250	900-1200	550-650
Heating rate (°C/s)	0.1-1	10-200	>1000	1-10
Residence time(s)	300-550	0.5-10	<1	0.5-20
Main Products	Bio-char	Bio-oil	Bio-oil	Bio-char + Bio-oil

2.1.3 Products from pyrolysis

The operating conditions during pyrolysis highly affect the final product. **Fast and flash pyrolysis** mainly produces **bio-oil** at a temperature range 850-1250 °C and very short residence time. Bio-oil produced in fast pyrolysis has a ratio of 60-75% but in flash pyrolysis, the ratio increases. As for **slow pyrolysis**, it mainly produces **biochar** at a temperature

between 550-950 °C for 1-4 hours. On the other hand, **intermediate** pyrolysis makes a balance between liquid and solid production [8].

2.2 Biochar

Biochar, also called charcoal, is the solid product from pyrolysis, or it is the carbonaceous residue after all volatile matter leaves the biomass as gasses and tar. It has an internal surface area of 500 to 1500 m²/g [13]. The properties of produced char depend on the feedstock type and operating conditions during pyrolysis. Generally, it is more favorable to operate at low temperature and high residence time to produce biochar [8]. The produced char from pyrolysis has intermediate pores, which improve its ability for filtration and adsorption of pollutants.

2.3 Factors affecting Biochar production

2.3.1 Type of biomass:

Biochar can be manufactured from agricultural precursors with a high carbon and low inorganic content. Agricultural waste is being used due to its abundance, low economic value, low ash content, acceptable hardness, rigidity and its disposal is an environmental concern [14]. The most common wastes used for the production of char are wood, coconut shell, bituminous coal, peat, etc [13]. The final properties of the carbon will depend significantly on the nature of the starting material [13]. Formation of Biochar is enhanced by cellulose and lignin content. The studies show that the highest lignin content in the biomass waste increase the biochar production in addition to increase the micropores surface area [6]. Lignin, cellulose, and hemicelluloses decomposed in different ranges of temperature. Decomposition of hemicelluloses occurs in a range between 220-315°C, while cellulose decomposes in a

range between 315-400°C. Finally, lignin is decomposed at a temperature more than 400 °C [15]. At low temperature, cellulose decomposes to a stable a hydrocellulose material, which means a higher char production. However, it is converted to volatile products at high temperature [8]. In summary; lignin is the major contributor in char production. By comparing between olive husk, corncob and tea waste, the olive husk produced the largest amount of biochar since it has the most lignin content [8]. Biomass with low water content is most suitable for pyrolysis, moisture content more than 30% require drying before pyrolysis in order to prevent energy loss in moisture removal. A biomass of less than 5% moisture content gives higher production of char [8]. It is important to know the constituent of different biomass in order to ensure that biomass is suitable for char production, Table 2.2 shows the proximate and ultimate analysis of the most biomass using for char production.

Table 2.2 Proximate and ultimate analysis of the most biomass used in char production [16].

Agricultural waste	Moisture % ww	Ash % ww	Volatiles % ww	C % ww	H % ww	O % ww	N % ww	S % ww
Olive tree pruning	7.1	4.75	-	49.9	6	46.4	0.7	-
Cotton stalk	6	13.3	-	41.23	5.03	34	2.63	0
Durum wheat straw	40	-	-	-	-	-	-	-
Corn stalks	0	6.4	-	45.33	6.15	41.11	0.78	0.13
Soft wheat straw	15	13.7	69.8	-	-	-	-	-
Vineyard pruning	40	3.8	-	47.6	5.6	41.1	1.8	0.08
Corn cobs	7.1	5.34	-	46.3	5.6	42.19	0.57	0
Sugar beet leaves	75	4.8	-	44.5	5.9	42.8	1.84	0.13
Barley straw	15	4.9	-	46.8	5.53	41.9	0.41	0.06
Rice straw	25	13.4	69.3	41.8	4.63	36.6	0.7	0.08
Peach tree pruning	40	1	79.1	53	5.9	39.1	0.32	0.05
Almond tree pruning	40	-	-	-	-	-	-	-
Oats straw	15	4.9	-	46	5.91	43.5	1.13	0.015
Sunflower straw	40	3	-	52.9	6.58	35.9	1.38	0.15
Cherry tree pruning	40	1	84.2	-	-	-	-	-
Apricot tree pruning	40	0.2	80.4	51.4	6.29	41.2	0.8	0.1

2.3.2 Heating rate:

The heating rate has a high influence on products characteristics of biomass pyrolysis. In pyrolysis of rapeseed, when the heating rate increase from 5 to 50 K/min the mass losses increase from 1.1 to 10 mg/min [17]. Also in pyrolysis of cherry sawdust the yield of biochar increases from 29.98% to 39.98% when the heating rate decrease from 10 to 5 °C/min [18]. Fast heating rate leads to quick fragmentation of biomass and produces a high amount of gasses [12], while the lower heating rate leads to produce more stable a hydrocellulose and increase char production [18].

2.3.3 Temperature:

Pyrolysis temperature has the most important effect after pyrolysis heating rate, and then pyrolysis residence time [16]. Increasing temperature usually increases the yield of liquids and gasses and thus, low yield of char. On the other hand, higher temperature produces higher char quality. That can be explained by primary decomposition of biomass occurring significantly at higher temperatures or through secondary decomposition of char residue. The secondary decomposition of the char at higher temperatures may also give some non-condensable gaseous products, which also contributes to the increase in gas yield. As the temperature of pyrolysis increased, the residence time of vapors of the primary degradation inside the cracked particles must be reduced [16]. The amount of fixed carbon of biochar produced from cherry sawdust increased from 59.59% to 61.29 % when the temperature increased from 450 to 800°C, while the yield decreased from 30.4% to 24.72% at heating rate 10°C/min [18]. However, the effect of temperature depends on biomass nature and composition, so it is difficult to find a suitable specific temperature for biochar production [8]. Table 2.3 shows the relation between pyrolysis temperature and biochar yield for different biomass types.

Table 2.3 Effect of pyrolysis temperature [8].

Biomass	Temperature range °C	Biochar yield %
Rice husk	400-600	33-25.5
Ferula Orientals	350-600	40.26-26.29
Corn cob	400-700	34.2-20.2
Sewage slug	350-950	52-39
Olive husk	450-1250	44.5-19.4
Corn cob	450-1250	30.6-5.7
Pine	300-450	58-26

2.3.4 Residence time:

The biomass should have a sufficient time to react in order to complete repolymerization of biomass constituents. In addition, sufficient time develops the macro and micro pores of Biochar [8]. Residence time and temperature do not affect the yield of biochar only, but also affecting physical, chemical, spectral, and morphological properties of biochar. When duration increases, yield, volatile matter and the original cell structure is reduced, but C, K and P contents increase, which give a high quality charcoal [19]. Another study shows that the biochar yield increases with the increase of residence time at high temperature, but at low temperatures, increasing residence time will decrease the biochar yield [8].

2.4 Activation

Char is being activated to increase the porosity and to widen the existed micropores and mesopores [20]. There are three types of activation:

2.4.1 Physical Activation

Carbonized material is exposed to an oxidizing gasses such as air, carbon dioxide CO₂, steam or a mixture of them under a temperature of 800-1100°C[21]. CO₂is usually used as an activation gas since it's clean, easy to handle and slow reaction rate at 800°C [16]. However, using steam is more efficient than CO₂ since it produces a higher surface area and faster conversion since the small size of water molecules cause diffusion through porous structure more effectively [6]. However, physically AC doesn't have satisfactory characteristics as an adsorbent or filter [16].

2.4.2 Chemical Activation

The carbonized material is impregnated with an oxidizing agent for dehydration by mixing or kneading with a concentrated solution of acid or base. The commonly activated chemicals are ZnCl₂, H₃PO₄, NaOH, KOH, and K₂CO₃ [16, 21]. These dehydrating agents prevent tar and other unwanted material to form in carbonization, which produce a higher percentage of carbon content. To acquire the final porous structure, chemical activation must be followed by thermal treatment of inert atmosphere. Chemical activation is performed at a lower temperature and part of the activation chemicals can be recovered, zinc salts and phosphoric acid for instance [16].

Comparing between chemical and physical activation, the priority for chemical activation due to lower activation temperatures, shorter treatment time, larger surface area and micro porosity, and a higher yield of AC production [6].

2.4.3 Physiochemical activation

A combination of the first two activation processes [6]. It's used to prepare granular AC of a very high surface area and porosity for specific applications, gasoline vapor control for example.

2.5 Activated carbon

AC is classified into four main groups according to its structure including granular activated carbon (GAC), powdered activated carbon (PAC), activated carbon fibers (ACF), and activated carbon cloths (ACC). GAC is usually prepared from hard materials of high rigidity and large particles retained on mesh #80, used as filler in columns, can be regenerated after use. When raw material particles are small, PAC is produced. For having small volumes, highly efficient adsorption occurs, even though settling and removal are slower in PAC than GAC. It's disposed of after using. ACF is manufactured from homogeneous polymeric raw materials, has a mono dispersed pore size distribution. The thin fiber shape develops intra-particle adsorption. Therefore, the contact efficiency between the media and the adsorbent is enhanced. "ACC were initially developed using as precursors phenolic or viscose rayon and are considered to be excellent adsorbents due to their low-pressure drop during the process, high contact efficiency and flexibility"[14].

AC has a number of unique characteristics such as large internal surface area, chemical properties, and good accessibility of internal pores for adsorption. According to IUPAC definitions, three groups of pores can be identified.

- 1- Macropores (above 50 nm diameter)
- 2- Mesopores (2-50 nm diameter)
- 3- Micropores (Under 2 nm diameter) [13].

The pores properties include the total pore volume, diameter, and size distribution. They are a function of the rate of heating, final temperature, time it's exposed to the final temperature, the type of activating agent, biomass properties and its history of carbonization [21].

Materials with a high content of lignin produce AC of macropores structure, while precursors of higher content of cellulose develop AC with micropores structure [16]. However, the surface area of the AC was less important in adsorption than the pore size distribution [20] and that AC with micropores and mesopores has higher removal efficiency than AC of macropores due to a higher diffusion rate of H₂S and the development of the deposition of sulfur product in mesopores.

2.6 Literature review on activated carbon production

Many researchers produced AC from agricultural residues after carbonization and activation for different applications, Table 2.4 shows different biomass wastes used for this purpose and summarizes the operating conditions during pyrolysis, activation methods used, characteristics of produced AC and the application that AC has been used for.

Table 2.4 Literature review on activated carbon production.

Raw Material	Particle size	Pyrolysis				Activation	S _{BET} m ² /g	Pore vol cm ³ /g	Pore size	Application (adsorbate material)	Ref
		Type	Temp °C	Residence Time	Heating Rate °C/min						
Bituminous Coal	0.147–0.295 mm	Slow	600 - 800	1-3 h	21	Physical (steam) + Chemical (ZnCl ₂)	400	-	-	H ₂ S	22
Oat hulls & Corn Stover	-	Fast	500	1.5 s	-	Physical (steam)	Oat(349-625) Corn (311-442)	Oat 92.4% corn 88.7%	-	-	23
Eucalyptus	25 mm	Slow	500	3 h	10	Chemical (K ₂ CO ₃)	535	-	-	Methylene-blue phenol	24
Walnut shell, Olive Stone	1-3 mm	Slow	600	1 h	-	Chemical (KOH)	-	-	12 μm	Iodine	25
Oil-Palm Stone	2-2.8mm	Slow	600	2 h	10	Physical (CO ₂)	176	0.11	-	SO ₂	26
Pine Cones	-	Slow	500	1 h	8	Chemical (H ₃ PO ₄)	1094.1	0.701	-	Lead	27
Corn cob	-	Slow	500	0.5 h	10	Chemical (ZnCl ₂)	970	0.288	-	Acid dye	28
Groundnut Shell	-	Slow	400	0.5 h	-	Chemical (ZnCl ₂)	-	-	-	malachite green	29
Almond Shell	1.5–2.0 mm	Slow	400	1 h	4	Physical (CO ₂)	1005-1315	-	-	-	30
Macadamia Nutshell	212-300 500-600 mm	Slow	700	1,2,3 h	-	Chemical (ZnCl ₂) (KOH)	1700 1100	0.7 0.5	-	-	31
Coffee Husk	-	Slow	550 250	3 h	-	Chemical (ZnCl ₂) (FeCl ₃)	1522 1374	-	-	Methylene-blue phenol	32
Anaerobic Digestion By-Product	-	Slow	400 – 800	-	-	Activated	317.6	0.2198	-	H ₂ S	20
Oak	Less than 1mm	Fast	500	-	-	Physical (CO ₂)	642-985	0.41-0.64	-	-	33
Corn Hulls							902-1010	0.68-0.89			
Corn Stover							432-712	0.33-0.54			

Chapter Three

Literature Review

Adsorption of Hydrogen Sulfide

3.1 Introduction

Adsorption process is used worldwide mainly with activated carbon in different gas and liquid treatment applications. One of these applications is H₂S removal from biogas. Biogas purification is a necessary process in biogas plant for higher electrical generation efficiency. This chapter studies the adsorption process and the relation between adsorbent and adsorbate.

3.2 Adsorption

Adsorption is a process in which particles (adsorbate) are separated from a fluid stream to a porous solid (adsorbent) surface exposed to the fluid. The adsorbate is then concentrated on the porous solid surface. The fluid can be passed through a fixed bed full of small solid particles of a highly surface area to obtain high adsorption efficiency. The fixed bed will reach saturation after a period of time, then, there will be no adsorption and the efficiency will decrease to 0% where desorption process occurs. The adsorbate can be recovered and the adsorbent then is ready for another cycle of adsorption. Adsorption can be applied for the separation of a liquid/gas mixtures or removal of air and water pollutants. In gas, especially, adsorption is applied for dehumidifying gas, eliminating the odor or pollutants from gas stream, or recover valuable solvent vapors from the steam. Removal of sulfur compounds from natural gas or biogas is one of the applications of gas phase adsorption.

Many adsorbents used in other applications of separation, sharing main properties in common including its porous structure of fine pores, pores volume of 50% of total particle volume and a shape of small pellets, beads, or granules of 0.1-12 mm in size. The adsorption inside the solid pores usually forms a monolayer. However, multi-layers sometimes occur.

3.3 Equilibrium Relations for Adsorbents

The equilibrium between the adsorbate concentration in the fluid phase (c , Kg adsorbate/ m^3) and its concentration on the solid surface (q , Kg adsorbate/Kg adsorbent) can be represented by the adsorption isotherm. Figure 3.1 presents some common types of adsorption isotherm including Linear, Freundlich, and Langmuir.

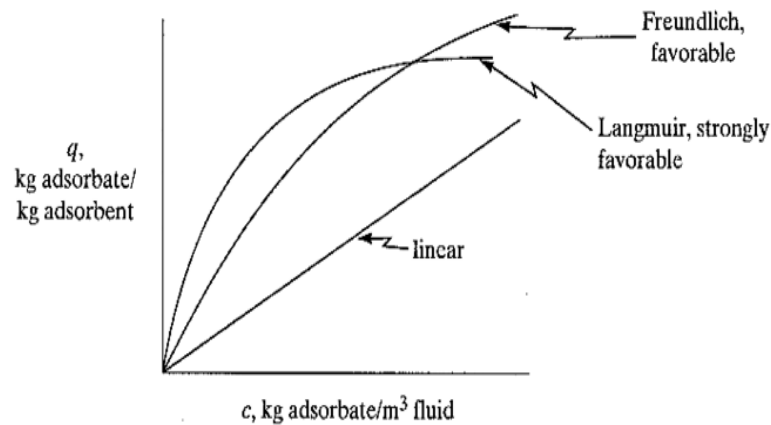


Figure 3.1 Common Types of Adsorption Isotherms

3.2.1 Linear isotherm

Linear isotherm occurs when the equilibrium concentrations follow a linear relationship as equation 3.1 shows. Linear isotherm is used in the dilute region to approximate data.

$$q = K * c \quad (3.1)$$

Where K is a constant determined experimentally (m^3/kg adsorbent)

3.2.2 Freundlich isotherm

Particularly useful for liquids to approximate data for physical adsorption by the empirical equation 3.2

$$q = K * c^n \quad (3.2)$$

Where K and n are constants determined experimentally. When a log-log curve plotted of q vs. c, the slope then is the exponent n. This equation is sometimes used to correlate data for hydrocarbon gasses on activated carbon.

3.2.3 Langmuir isotherm

A theoretical basis given in equation 3.3 represent Langmuir isotherm,

$$q = \frac{q_o * c}{K + c} \quad (3.3)$$

Where K (Kg/m^3) and q_o ($\text{Kg adsorbate}/\text{Kg solid}$) are empirical constants. The Langmuir isotherm assumes that only a monolayer is formed, the adsorption is reversible and reaches the equilibrium condition. It also assumes that there are a certain number of active sites for adsorption. The slope is obtained by plotting $1/q$ vs. $1/c$, and is equivalent to K/q_o , whereas the intercept in this system is equivalent to $1/q_o$.

3.4 Breakthrough Curve

Adsorption can occur in batch or continuous process, batch adsorption mostly used for liquids when quantities treated are small in amount. Whereas continuous adsorption is a

widely used method for adsorption of solutes from liquids or gasses by using a fixed bed of particles. In this case, the concentration of adsorbate in the fluid phase and in the solid phase changes with time and position in the bed. The difference in concentration is the driving force for mass transfer between the fluid and solid phases.

At the beginning of adsorption process, the concentration in a fluid phase drop to zero and adsorption occur in the layer of particles near to inlet. The concentration on solid phase will increase continuously until the ratio of solute concentration between outlet and inlet fluids (c/c_0) reach 1 after time interval, which means this layer of particles become saturated as t_1 in Figure 3.2 shows, so mass transfer takes place in the next layer of solid particles and so on. Until all of the particles become saturated and mass transfer stops, this process is shown in Figure 3.2. The zone where the change in concentration occurs is called mass transfer zone.

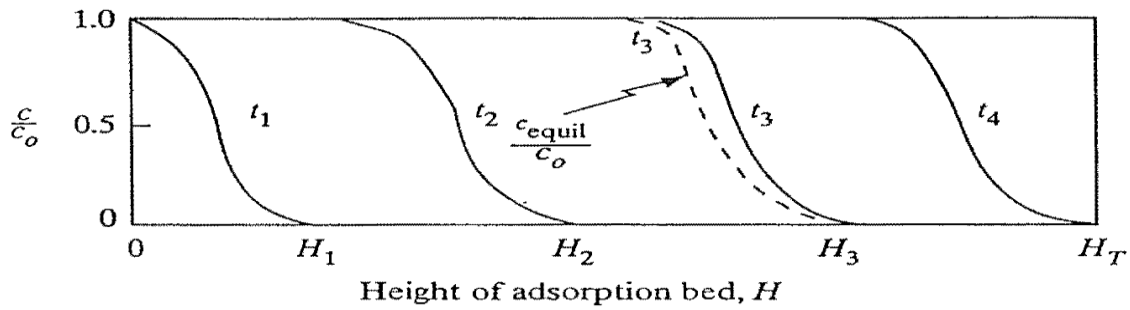


Figure 3.2 Concentration profile for adsorption process in a fixed bed at various positions.

The relation between the concentration of fluid leaving the bed and time can be represented in a breakthrough curve. As the solution continues to flow at a given time when almost half of the bed is saturated with solute, the outlet concentration is still approximately

zero, as shown in Figure 3.3. 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 the outlet concentration reaches c_b , which is called the break point. The break point concentration represents the maximum concentration that can be discarded and is often taken as 0.01 to 0.05 for c/c_0 . After that, the concentration rises very rapidly up to point c_d , which is the end of the breakthrough curve. In this level, the bed becomes ineffective and c/c_0 reaches 1. That means the outlet concentration equal inlet concentration as shown in Figure 3.3.

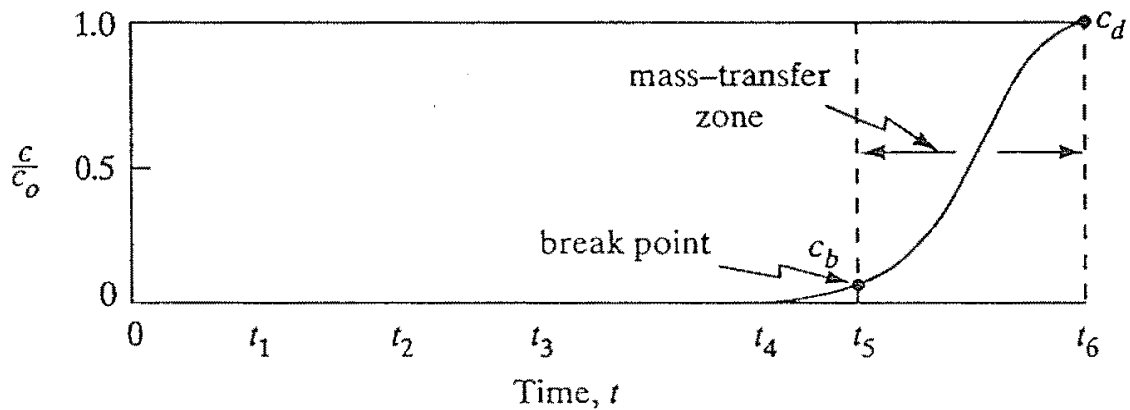


Figure 3.3 Breakthrough curve, concentration profile for adsorption process in a fixed bed at various times.

The removal of hydrogen sulfide from biogas has been a major concern for several years. Many published studies proved that the AC is a good adsorbent for H_2S . In reference [11], the author compares between activated carbon, zeolites and oxide adsorbent. The highest desulfurization efficiency is observed on activated carbons and their modified forms when H_2S outlet concentration was less than 1ppmv with efficiency 99%. The studies given in Table 3.1 discuss different factors affecting H_2S adsorption process.

Table 3.1 Literature review on adsorption of hydrogen sulfide.

Raw Material	Particle size or shape	Activation condition				Adsorption condition						Ref
		Material	Temp °C	Time	Ratio	D _{bed}	L _{bed}	Temp °C	AC mass	Flow rate	Inlet conc.	
Coconut shell	Granular 1.8-3.6 mm	O ₃ HNO ₃	-	-	-	1.2 cm	5.5 cm	10 30 45	3 g	150 cm ³ /min	1.01 % with N ₂	21
Coconut shell	Granular	NaOH KOH Na ₂ CO ₃ KI	100	30 min	-	12 mm	70 cm	30 30- 550	1 g	100 ml/min	-	35
Bituminous Coal	0.147–0.295 mm	Steam , ZnCl ₂			0.5-2.0	1.2 cm	5.5 cm	550	5.5 g	200 cm ³ /min	-	22
Commercial AC from rayon, Coconut shell	Fiber, granular	CO ₂ H ₂ O	1200 900	-	-	-	-	-	-	Batch reactor	-	36
Anaerobic Digestion Byproduct	-	Steam	850	-	-	-	-	-	-	-	-	20
Commercial	-	Without activation	-	-	-	9 mm	370 mm	-	-	0.5 L/min	3000 ppm	37
Coconut Shell	4×8US standard mesh size	KOH NaOH K ₂ CO ₃	Room temp	1 h	0.25 , 0.5 ,1 1.5 , 2	-	-	30-70	-	-	1000-5000 ppm	38
Commercial	Powder	N ₂ ,O ₂	900	6 h	-	38 cm	1 cm	23	1g	150 ml/min	200 ppm	39

Different raw materials of AC used in H₂S removal after physical or chemical activation or without any activation. One of the most biomass waste used for this purpose is coconut shell due to its high cellulose and lignin content, which produce a highly efficient AC.

Activation of carbon affects highly the adsorption process. In reference [38], the author compares between impregnated and unimpregnated carbons. The adsorption capacity of unimpregnated AC was 1.5 mg/g. Physical adsorption occurs in this case, where molecules are weakly bonded by van der Waals forces. As a result, the highest capacity of unimpregnated AC was 1.67 mg /g in reference [39].

Impregnation of AC rises the adsorption capacity 12.3 times in NaOH impregnated AC and 13.5 times in K₂CO₃ AC. Adsorption, in this case, is chemical irreversible adsorption depends on the reaction between H₂S and the functional group on AC surface [38].

Different chemicals used to activate carbon but H₂S is an acidic gas so the presence of a basic group on AC surface will improve the adsorption capacity [38]. The surface acidification of AC was studied and proved that H₂S removal efficiency is reduced because H₂S cannot be dissociated with acidic conditions [40]. As a result, basics are favorable as activating material for H₂S removal and the most basics used are KOH, NaOH, K₂CO₃ and KI.

Adsorption of H₂S is affected by local pH within pore system which affected by pore size and acidic groups location. Physical adsorption can exist at low pH while chemical

adsorption exists at high pH and H₂S oxide to polymeric sulfur in this case [37]. pH less than 5 decreases the H₂S capacity [40].

Break through capacity was 20 mg/g for K₂CO₃ AC and 10.9 for NaOH. When NaOH to carbon mass impregnation ratio increases, the adsorption capacity decreases. That might be due to pores blockage by NaOH. The same happens when KOH impregnated ratio increases more than 1.5. However, in the case of K₂CO₃, the adsorption capacity increases to 35mg/g when the ratio increases to two [39]. Coconut samples were activated with NaOH, KOH, and K₂CO₃. The best adsorption capacity was for AC impregnated with K₂CO₃ [40].

Decreasing H₂S concentration at the inlet increases the removal efficiency as low concentrations slow down concentration kinetic and decreasing surface acidification [40]. The adsorption capacity had dropped when the H₂S influent concentrations increased from 1000 to 5000 ppm [38].

The flow rate is an important factor as it determines the contact time between gas and AC. Adsorption capacity increases with decreasing flow rate due to longer contact time [38].

Different amounts of AC were used in reference [38] to study the effect of AC amount. Increasing AC from 4 to 7 grams led to an increase in the total surface area and adsorption capacity. Longer time is taken to reach break through concentration at $c/c_0 = 0.05$.

Chapter Four

Experimental Work

4.1 Materials

Almond shells and eucalyptus were obtained from home garden, Hebron, Palestine. Coffee grains wastes were also collected from home kitchen, Hebron, Palestine. Two chemicals were used for activation; $ZnCl_2$ and KOH (ALBEMARLE, Louisiana, Florida, USA). Biogas was obtained from AL-Jebriny biogas plant in AL-Dhahreieh, Hebron, Palestine.

4.2 Activated Carbon Production

Almond shells, eucalyptus and coffee grains were collected and washed well with tap water to remove any impurities then, dried in a drying oven (Daihan LabTech Co., Ltd., Korea) at a temperature of $105^{\circ}C$ for 24 hours. The samples were then smashed using stainless steel mill and sieved using the auto sieve analysis shaker for 15 minutes. Meshes # (10, 18, 40, 60 and 140) were used in sieving process. After that, the samples retained on mesh #140 that has an opening size of 0.105 mm were chosen for subsequent studies in order to obtain a uniform particles size.

Samples were then filled in porcelain crucibles for pyrolysis process. To make sure that pyrolysis occurs in the absence of oxygen, the samples were pressed well to reduce the voids that may present between particles and contain oxygen. Porcelain crucibles were closed and covered by aluminum sheets. An isolated muffle furnace (labTech International Ltd. East Sussex, UK) was used to pyrolyse the samples at a temperature of $500^{\circ}C$ for one hour.

Samples then were activated with two different activation agents including KOH and $ZnCl_2$. Firstly, the activation reagent was added to the pyrolysed biomasses with a mass ratio of 1:4 (weight of activating agent to weight of sample) then, distilled water was added to the mixture with a volume equals 10 times of the pyrolysed sample weight. After that, solutions

were stirred and heated at 80°C, using a hotplate stirrer (labTech International Ltd. East Sussex, UK) until water was evaporated in a range time 1-2 hours. Next, the drying oven was used to dry samples completely at 105 °C for 24 hours.

The three biomasses were weighed before and after pyrolysis to obtain yield as shown in equation 4.1.

$$\text{yield} = \frac{\text{mass before pyrolysis}}{\text{mass after pyrolysis}} \quad (4.1)$$

4.3 Adsorption Tests

A fixed bed filter with a dimension 1cm internal diameter and 12 cm height was used in adsorption tests (see Figure 4.1 for a schematic diagram of setup) of H₂S removal. Two thin layers of a porous cloth with a thickness less than 1 mm were placed at the inlet and outlet of the filter in order to hold AC. The biogas from digester enters the upper bed inlet (1) then passes through AC layer where adsorption occurs (2). Then it leaves the bed to the sensor (ToxiRAE Pro, HONEYWELL, San Jose, California, United status) for measuring H₂S outlet concentration with time, the outlet concentration was measured every minute until outlet concentration reaches its inlet concentration.

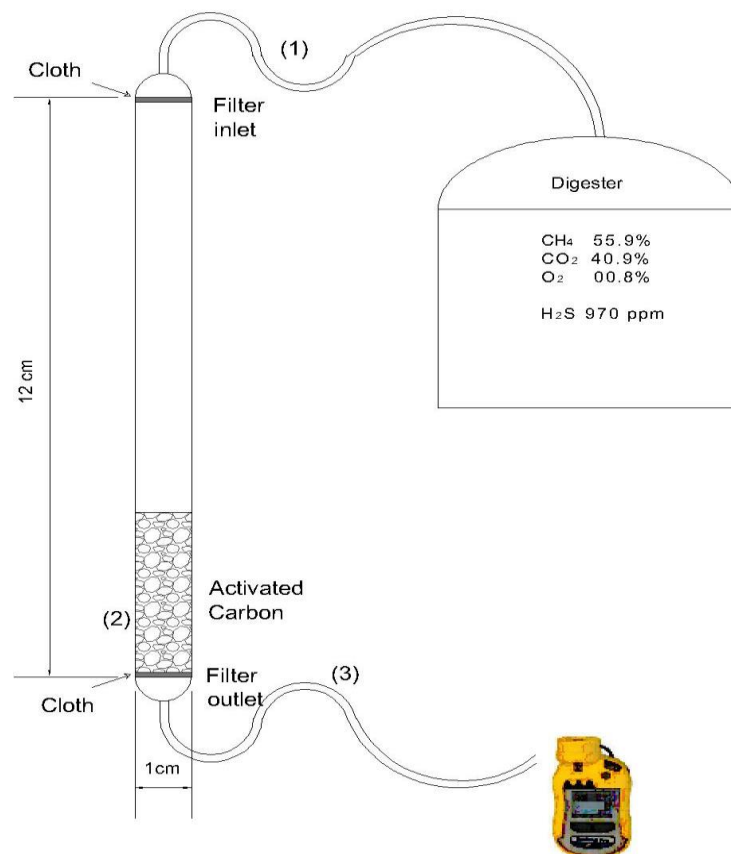


Figure 4.1 Schematic Diagram for H₂S Adsorption Test.

The flow rate of biogas was measured using fluid displacement method, in which an empty balloon was placed at the end of the inlet pipe and left to be filled with biogas for a certain time. The filled balloon was then immersed in water bath. The displaced volume of water was measured and flow rate was calculated using equation 4.2:

$$\text{flow rate} = \frac{\text{volume of displaced water}}{\text{time to fill balloon}} \quad (4.2)$$

4.3.1 Effect of biomass precursor type

The three types of precursors (Almond shells, eucalyptus and coffee grains) activated with KOH were used to measure biomass effect on H₂S removal efficiency. The bed height was fixed at 2cm and the flow rate was 1.5 L/min. The outlet concentration of H₂S was then measured with time until it reaches the inlet concentration.

4.3.2 Effect of activation reagent

To study the effect of activation reagent on H₂S removal efficiency, a bed height of 2 cm of eucalyptus activated with KOH or ZnCl₂ was used and the flow rate was 1.5 L/min.

4.3.3 Effect of bed height

To study the effect of bed height, 2, 4, 6 and 8 cm of coffee grains activated with KOH were used and the flow rate was 1.7 L/min.

4.4 Data Analysis

The data obtained from experimental work was analyzed according to following methods and equations.

The type of flow determined by calculating Reynold's number for flow through a packed bed with void ratio ϵ according to equation 4.3 [41].

$$Re_p = \frac{\rho * U * D}{(1 - \epsilon) * \mu} \quad (4.3)$$

The void ratio for each sample was calculated as shown in equation 4.4 [42].

$$\epsilon = \frac{V_V}{V_T} \quad (4.4)$$

Where V_V is the volume of voids between particles and V_T is the total volume of the sample. Fluid saturation method was used to determine the voids volume [42], where a specific amount of dry sample was weighted. Then, tap water was added to the sample until saturation, wet sample was put in a filter paper to expose any excess water. Then, the saturated sample was weighted. The difference between dry and saturated samples weights represents the weight of water in pores. Volume of pores can be represented by water volume in pores that equals weight of water divided by water density. After that fluid displacement method was used to determine the total volume where the saturated sample was immersed in water. The volume of displaced water was calculated which equal the total volume.

Pressure drop for laminar flow through a bed of particles was calculated using (Carman–Kozeny equation) as shown in equation 4.5 [41].

$$\frac{\Delta p}{H} = 180 \frac{\mu U}{x^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} + 1.75 \frac{\rho U^2}{x} \frac{1-\varepsilon}{\varepsilon^3}$$

(4.5)

Where,

ρ : Gas density (Kg/m³)

U: superficial fluid velocity through the bed (m/s)

D: Bed diameter (m)

μ : fluid dynamic viscosity (pa.s)

ε : void fraction (dimensionless)

Δp : pressure drop (pa)

H: height of the bed (m)

x: particle diameter (m)

Removal percentage of H₂S was calculated by equation (4.6) [34], where the adsorption capacities were calculated by equation (4.9).

$$\% \text{ removal} = \frac{c_0 - c}{c_0} * 100 \%$$

(4.6)

Where c_0 and c are the inlet and outlet concentration of H₂S (ppm) respectively.

As shown in the figure 4.2, the mass balance of H₂S is

$$\text{Total adsorption amount} = \text{total accumulation} = \text{input} - \text{output}$$

(4.7)

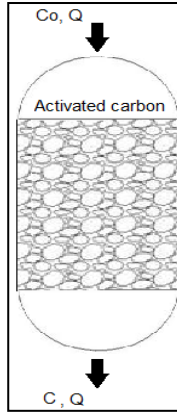


Figure 4.2: AC packed bed input and output.

$$\text{Rate of accumulation (R)} = c_o * Q - c * Q$$

$$\int_0^{\infty} R dt = \int_0^{\infty} (c_o * Q - c * Q) dt$$

$$\int_0^{\infty} R dt = Q c_o \int_0^{\infty} \left(\frac{c_o - c}{c_o} \right) dt$$

$$\text{Total accumulation} = \int_0^{\infty} \left(1 - \frac{c}{c_o} \right) dt \quad (4.8)$$

The integral $\int_0^{\infty} \left(1 - \frac{c}{c_o} \right) dt$ can be obtained from the shaded area of the breakthrough curve as shows in figure 4.3.

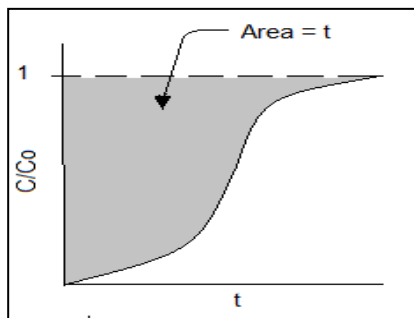


Figure 4.3 : Breakthrough curve.

The adsorption capacity of AC can be obtained from equation (4.9)

$$q = \frac{\text{total adsorption amount}}{m} \quad (4.9)$$

Where,

c_o : Inlet concentration of H₂S (g/L)

c_e : Outlet concentration of H₂S (g/L)

q : Adsorption capacity of AC (mg H₂S/ g AC)

Q : Flow rate (m³/min)

t : Adsorption time (min)

m : Mass of AC used in adsorption (g)

Chapter Five

Results and Discussion

5.1 Yield of Pyrolysis Process

The yield of carbonization was calculated after pyrolysis was performed on the three biomasses and the results are shown in Table 5.1.

Table 5.1: Biomasses yield from pyrolysis process

Biomass	Yield (%)
Eucalyptus	35
Almond shells	28
Coffee grains	23

Formation of biochar is enhanced by cellulose and lignin content in biomass, the eucalyptus has the highest yield as it has the highest lignin and cellulose content (28% w/w and 59.8 % w/w respectively) [43]. While for almond shells lignin and cellulose content are (20.4% w/w and 50 % w/w) [44] and (23% w/w and 12% w/w) for coffee grains waste [45].

5.2 Bed characteristics

Table 5.2 shows the characteristics of AC bed and biogas used in the adsorption tests.

Table 5.2: Characteristics of AC bed, biogas and operating conditions.

Variable	Symbol	Value	Unit
Density (biogas)	ρ	1.17	Kg/m ³
Dynamic viscosity (biogas)	μ	$1.26 \cdot 10^{-5}$	Pa.s
Flow rate	Q	1.5	L/min
Particles average diameter	x	$177 \cdot 10^{-6}$	m
Bed cross sectional area	A	$7.85 \cdot 10^{-5}$	m ²
Superficial velocity	U	0.318	m/s

5.3 Porosity and pressure drop

Table 5.3 shows the values of Reynold's numbers, void fractions, pressure drops per unit of height and the total pressure drop for 2 cm of the three biomasses samples.

Table 5.3: Void faction and pressure drop for eucalyptus, almond shells and coffee grains.

Biomass	ϵ	Re_p	$\Delta P/H$ (kpa/m)	ΔP (kpa)
Eucalyptus	0.7	984.28	7.01	0.14
Almond shells	0.63	798.07	14.23	0.28
Coffee grains	0.67	894.81	9.54	0.19

The table shows that decreasing the void fraction increases the friction and resistance to flow thus increases the pressure drop through the bed.

5.4 Adsorption Results

5.4.1 Effect of Biomass Precursor Type

The bed including cloth was firstly run empty without AC and the residence time (Q/V_{bed}) was calculated theoretically to be 0.3 second. However, experimentally the result shows that the outlet concentration of H_2S increased to reach its inlet concentration within 45 seconds (see Figure 5.1). That can be explained by delay of H_2S sensor since it consumes less than one minute to calculate the real concentration. Then the bed was filled with various types of AC activated with KOH Eucalyptus (Euc-KOH), Almond shells (Alm-KOH) and coffee grains (Cof-KOH) at a constant height of 2 cm and flow rate 1.5L/min.

A clear difference between the three types of AC in H₂S adsorption can be observed as shown in Figure 5.1 (a and b).

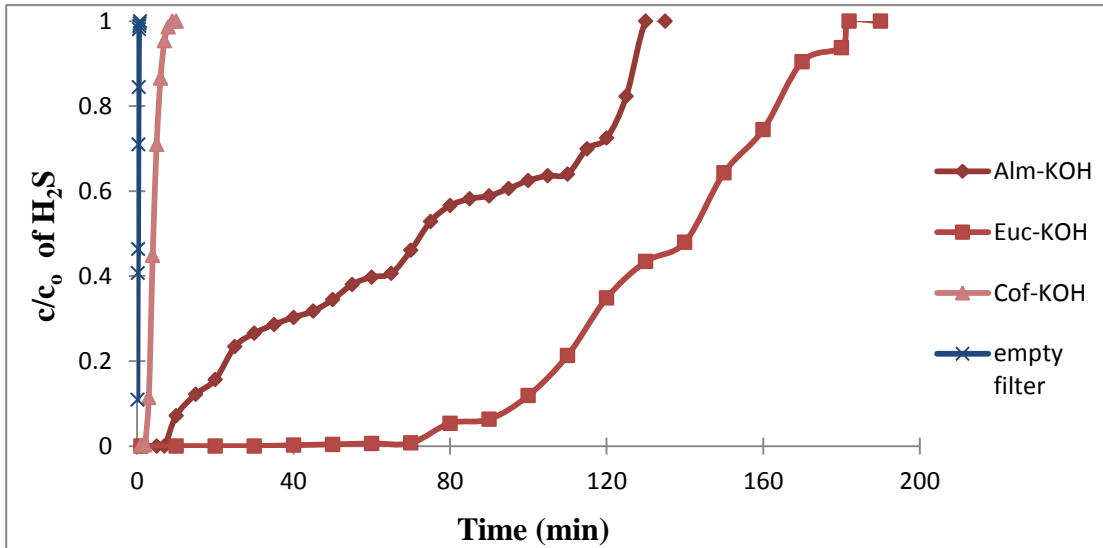


Figure 5.1 (a)

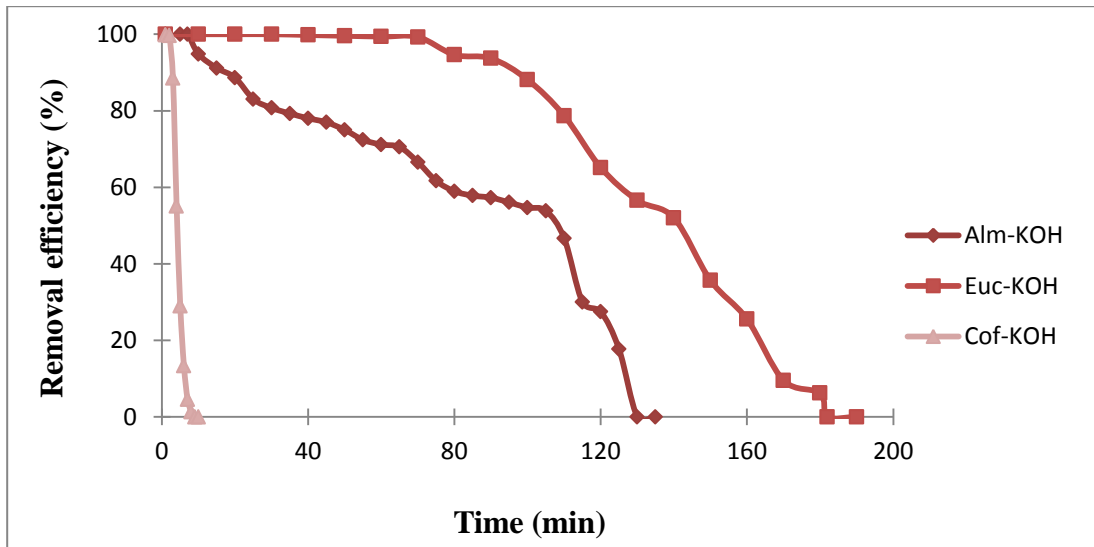


Figure 5.1 (b)

Figure 5.1: (a) Breakthrough curves, (b) Removal efficiency curves of H₂S through packed bed of AC made from eucalyptus, almond shells and coffee grains activated with KOH and empty filter. The experiments were performed at ambient air temperature, gas flow rate of 1.5L/min, bed height of 2cm and H₂S inlet concentration 970ppm.

At the beginning of the adsorption process, the concentration of outlet H₂S dramatically dropped to less than 10 ppm for the three samples; indicating high adsorption (removal) efficiency. With time, the outlet H₂S concentration increased at different rates depending on the AC sample. For instance, with Cof-KOH, the H₂S outlet concentration rapidly increases to reach its inlet concentration (i.e. 0% removal efficiency) after 9 minutes,. The Alm-KOH performed better than Cof-KOH as the outlet concentration remains around 0 (i.e. 100 % removal efficiency) for 7 minutes, then it gradually increases to reach its inlet concentration after 130 minutes (see Figure 5.1) the same was with removal efficiency which the highest removal efficiency was observed with Euc-KOH the outlet concentration remains around 0 with a removal efficiency of about 100 for 45 minutes then start to decrease slowly and reach 0 % after 182 minutes. The results indicated that the adsorption capacity of the ACs to the H₂S is different depending on the type of biomass precursor. Table 5.4 shows the adsorption capacities of three samples. The higher adsorption capacity indicates a better performance in adsorption process. Eucalyptus has the highest adsorption capacity which was 490 (mg H₂S/g AC). That means one gram of Euc-KOH can adsorb 490 mg of H₂S under the applied operational conditions.

Table 5.4: Adsorption capacities for almond shells, eucalyptus and coffee grains.

Biomass	Lignin content (% w/w)	Cellulose content (%w/w)	Adsorption capacity (mg H₂S/g AC)
Eucalyptus	28	59.8	490
Almond shells	20.4	50	230
Coffee grains	23	12	22

The results showed that, Euc-KOH has the best performance in H₂S adsorption, followed by Alm-KOH, Cof-KOH respectively. These results might be explained as follows. The microstructure of AC is strongly affected by original plant texture especially the lignin and cellulose content in which increasing the lignin content increases the macropores of AC

whereas increasing the cellulose content increases the micropores where the adsorption mainly takes place. As eucalyptus has the highest cellulose content (see Table 5.4) its adsorption capacity was the highest.

5.4.2 Effect of Activation Reagent

The pyrolysed eucalyptus was activated with ZnCl_2 and compared with KOH at the same operating conditions. Figure 5.2 shows break through curves and removal efficiency of H_2S .

The outlet concentration remained zero with a removal efficiency of 100% for 30 minutes for both of Euc- ZnCl_2 and Euc-KOH (see Figure 5.2). However, removal efficiency reached 0 after 70 minutes with Euc- ZnCl_2 instead of 182 minutes with Euc-KOH. As well as, the adsorption capacity decreased from 490 to 160 mg $\text{H}_2\text{S}/\text{g}$ AC when KOH replaced with ZnCl_2 .

The difference in efficiency can be explained by the higher chemical affinity of H_2S for KOH than ZnCl_2 . Since KOH is alkaline, it has a high reactivity to the diproton acidic gas H_2S . The reactions are expressed in equation 5.1 [46].



Studies indicate that chemical adsorption is the major factor affecting the adsorption process in alkaline AC [47]. AC activated with ZnCl_2 resulted in greater mesoporosity while microporosity is major in AC activated with KOH [48].

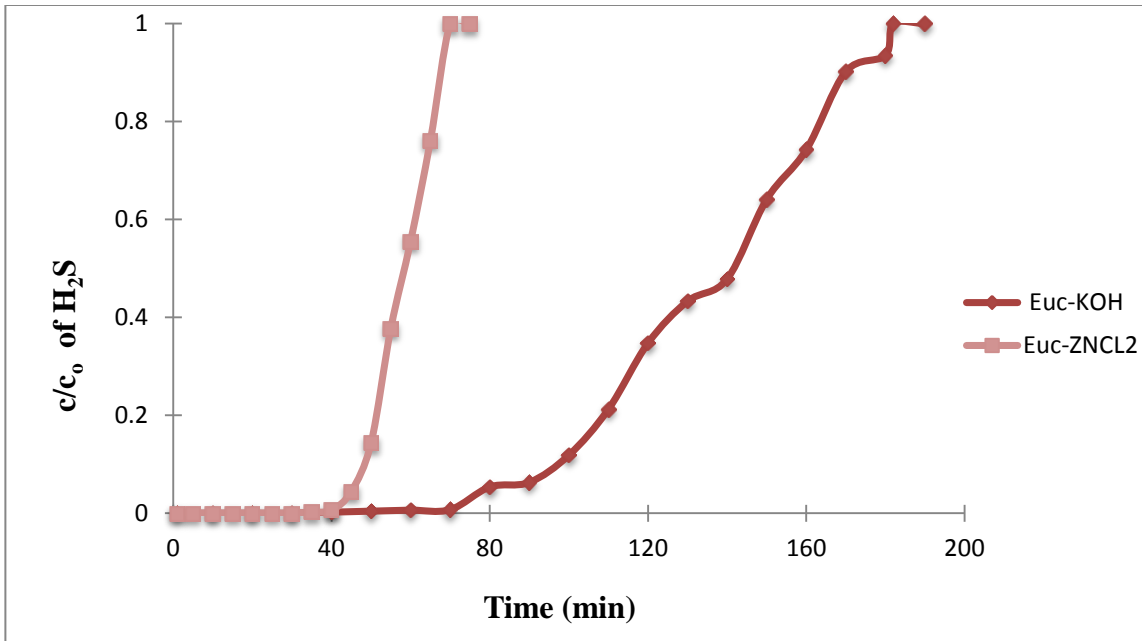


Figure 5.2 (a)

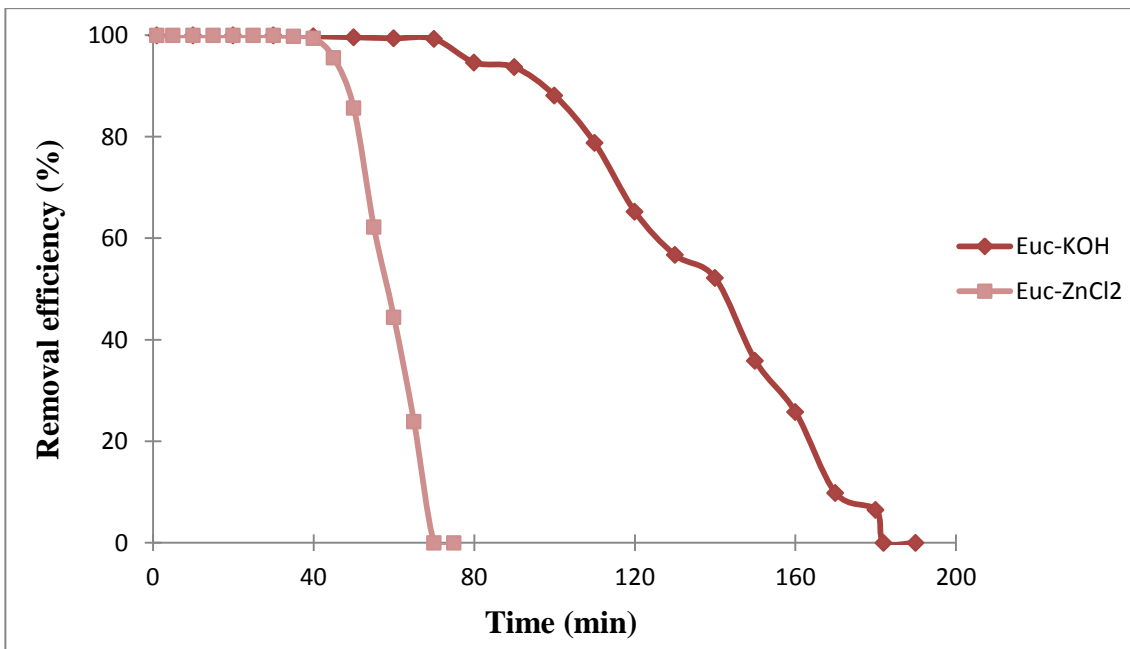


Figure 5.2 (b)

Figure 5.2: (a) Breakthrough curves, (b) Removal efficiency of H₂S curves through packed bed of AC made of Euc-KOH and Euc-ZnCl₂. The experiments were performed at ambient air temperature, gas flow rate of 1.5L/min, bed height of 2cm and inlet H₂S concentration 970ppm.

5.4.3 Effect of Bed Height

To study the effect of AC bed height, a new adsorption test was implemented on Cof-KOH at a flow rate 1.7 L/min and inlet H₂S concentration 930 ppm. 2, 4, 6 and 8 cm were used. The breakthrough curves of four samples are shown in Figure 5.5.

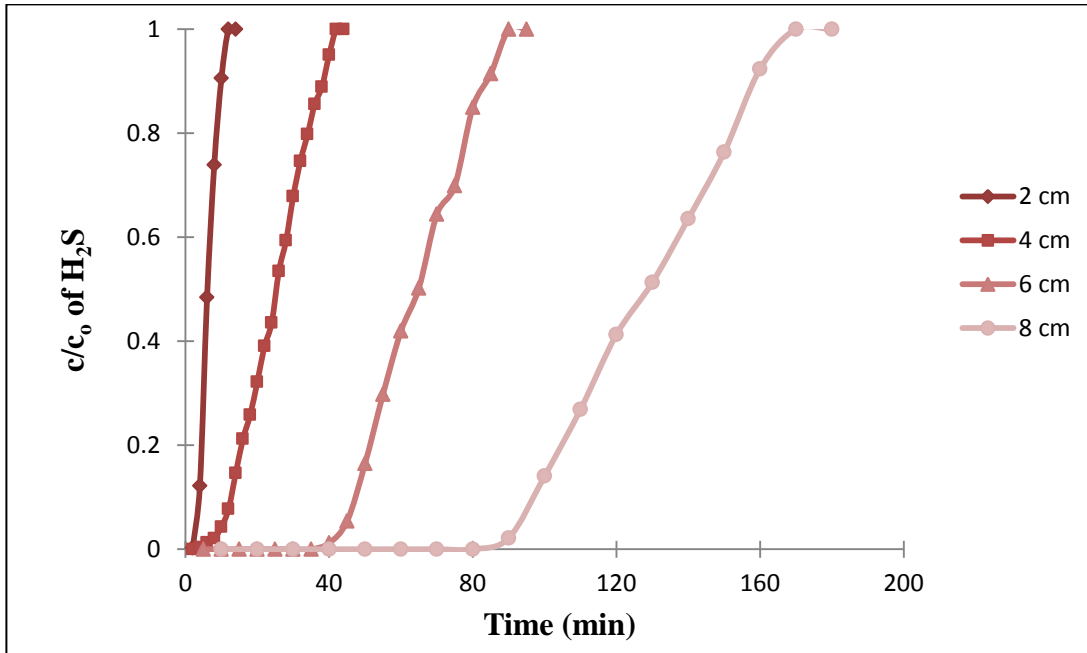


Figure 5.3: Adsorption breakthrough curves of H₂S through packed bed of AC made of Cof-KOH. The experiments were performed at ambient air temperature, gas flow rate of 1.7L/min, pressure drop of 9.36 kpa/m, H₂S inlet concentration 930 ppm and heights of 2, 4, 6 and 8 cm

As shown in Figure 5.3, with 2 cm Cof-KOH the c/c_0 ratio increased rapidly from 0 to 1 within 12 minutes but with increasing the bed height to 4 cm the ratio take 42 minutes to reach 1. With increasing the height to 6 cm the ratio remained zero for 35 minutes and increased gradually to reach 1 within 90 minutes. Finally, with 8 cm the ratio remained zero for 80 minutes and increased gradually to reach 1 within 170 minutes. Increasing the amount

of AC affect strongly on the adsorption of H_2S , Figure 5.6 shows the effect of AC bed height on adsorption capacity.

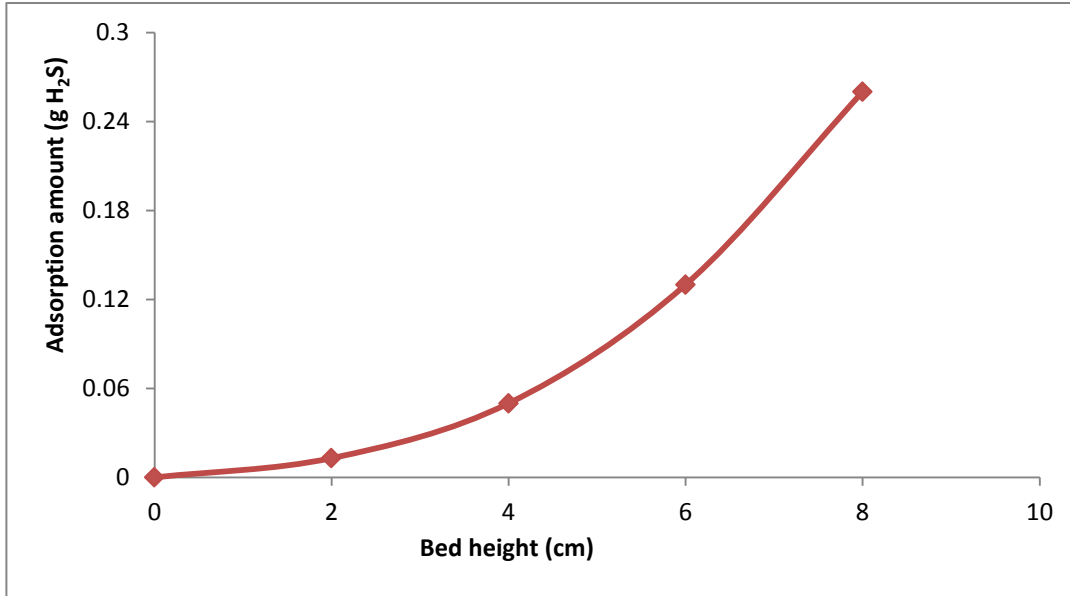


Figure 5.4: AC bed height versus the adsorption amount of H_2S

Figure 5.4 shows that increasing the amount of AC increase the total surface area and thus the total number of adsorption active sites. Furthermore, a longer AC bed provides a longer contact time between adsorbent and adsorbate that consequently increases the probability of adsorption.

Conclusion

In the current study, the technical feasibility of removing H_2S from biogas through packed bed of synthesized AC prepared from biomass waste was investigated. The findings revealed that the AC could be successfully synthesized from biomass waste. In addition, the technical feasibility of H_2S adsorption on the synthesized AC has been confirmed. Yield of carbonization was studied and showed that highest yield for eucalyptus then almond shells and finally coffee grains, their results were 35%, 28%, 23% respectively. The relation between removal efficiency of H_2S and the type of biomass, activation agent and the amount of AC used in the bed was studied. Time needed for outlet concentration of H_2S to reach its inlet concentration was 182, 120, 9 minutes for eucalyptus, almond shells and coffee grains respectively. As for chemical reagents study, eucalyptus activated with $ZnCl_2$ needed 70 minutes comparing to 182 minutes for KOH. Higher adsorption capacity achieved when increasing the amount of AC. Removal efficiency reached 0 after 12, 42, 90 and 170 minutes for 2, 4, 6, and 8 cm of Cof-KOH respectively.

Recommendations

1. Eucalyptus and almond shells are recommended to be used as efficient low cost adsorbents for gas adsorption applications.
2. We recommend AL-Jebriny Company to use local synthesized AC for biogas purification.
3. Chemical activation is preferred for activation as the required equipments are available and it's a cheap method.
4. The study of chemical activation to carbonized biomass ratio can be studied in further research.
5. Activated carbon can be studied as an adsorbent for other gases or liquids from other industries.

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