

**ACTIVATED CARBON (AC) PRODUCTION FROM SPENT MUSHROOM
SUBSTRATE (SMS) FROM FROZEN FOOD INDUSTRY**

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**BACHELOR OF CHEMICAL ENGINEERING
UNIVERSITI MALAYSIA PAHANG**

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

DISEMBER 2016

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree

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Date : JANUARY 2016

Dedicated to my beloved parents, siblings, teachers and my friends.

Thank you so much for always being there for me through thick and thin.

ACKNOWLEDGEMENT

I would like to express my special appreciation and thanks to my supervisor, Dr. Sunarti. You have been a brilliant mentor for me. I would like to thank you for your never ending support during my tenure as research student under your guidance, for giving insightful comments and suggestions of which without it, my research path would be a difficult one. Your advice on my research has been valuable. My fullest appreciation goes as well to my co-supervisor, PM Ir. Dr. Norazwina for her idea and support from the beginning till the end of my research.

A special thanks to my family. Words cannot express how grateful I am to my mother, father, and siblings for the love and support throughout these years. Your prayer for me was what sustained me this far. I would like to express appreciation to my research mate who always be my support in the moments in need.

I am also indebted to the Ministry of Higher Education and Universiti Malaysia Pahang for funding my study.

I would also like to thank all of my friends who supported me in writing, and motivate me to strive towards my goal. I am sincerely grateful to the staffs of Chemical Engineering and Natural Resources Faculty who helped me in many ways and made my stay in UMP pleasant and unforgettable.

ABSTRACT

Agriculture Industry in Malaysia has evolve entirely over the last decade due to the advancement in science and technology in these modern era. Globally, mushroom trade has shown an increasing trend over the last three decades. Nevertheless, Malaysia's mushroom industry had also shown an upward trend recently. Thus, the increasing of mushroom production in Malaysia also has led to the increase of the mushroom waste such as the spent mushroom substrate (SMS). It is estimated that for every kilogram of mushroom grown, about 4 to 5 kg of SMS is being produced. Since the SMS has high potential to be converted to activated carbon (AC) by using the pyrolysis method and chemical activation simultaneously, thus these study is crucial to identify whether it is suitable for the AC derived from these SMS to be used in the daily life or industrial application especially in the waste water treatment as the AC has a very excellent adsorption properties. In order to characterize the AC produce, the Surface area analyzer (BET), Scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analyzer (TGA) is use to analyze the AC's properties. It is expected that the AC produce from the SMS is suitable to be use in the industrial waste water treatment and other application since the SMS have high content of carbon compound that can be converted to AC by pyrolysis and chemical activation method.

ABSTRAK

Pertanian Industri di Malaysia mempunyai berkembang sepenuhnya sepanjang dekad yang lalu disebabkan oleh kemajuan dalam bidang sains dan teknologi di era ini moden. Di peringkat global, perdagangan cendawan telah menunjukkan trend yang meningkat sejak tiga dekad yang lalu. Walau bagaimanapun, industri cendawan di Malaysia juga telah menunjukkan peningkatan baru-baru ini. Oleh itu, peningkatan pengeluaran cendawan di Malaysia juga telah membawa kepada peningkatan sisa cendawan seperti cendawan substrat dibelanjakan (SMS). Adalah dianggarkan bahawa bagi setiap kilogram cendawan ditanam, kira-kira 4 hingga 5 kg SMS sedang dihasilkan. Sejak SMS itu mempunyai potensi yang tinggi untuk ditukarkan kepada karbon diaktifkan (AC) dengan menggunakan kaedah pirolisis dan pengaktifan kimia secara serentak, dengan itu kajian ini adalah penting untuk mengenal pasti sama ada ia adalah sesuai untuk AC diperolehi daripada SMS ini untuk digunakan dalam kehidupan harian atau aplikasi industri terutamanya dalam rawatan air sisa sebagai AC mempunyai ciri-ciri penyerapan sangat baik. Dalam usaha untuk mencirikan hasil AC, penganalisis kawasan permukaan (BET), mikroskop imbasan elektron (SEM), jelmaan Fourier spektroskopi inframerah (FTIR), dan penganalisa Termogravimetri (TGA) adalah digunakan untuk menganalisis sifat AC. Ia dijangka bahawa hasil AC daripada SMS adalah sesuai digunakan dalam rawatan air sisa industri dan aplikasi lain sejak SMS yang mempunyai tinggi kandungan sebatian karbon yang boleh ditukar ke AC dengan kaedah pirolisis dan pengaktifan kimia.

TABLE OF CONTENTS	PAGE
SUPERVISOR'S DECLARATION	ii
STUDENT'S DECLARATION	iii
ACKNOWLEDGEMENT	v
ABSTRACT	vi
ABSTRAK	vii
TABLE OF CONTENTS	viii
LIST OF FIGURES	x
LIST OF TABLES	xi
LIST OF ABBREVIATIONS	xii
CHAPTER 1 INTRODUCTION	
1.1 Background	1
1.2 Motivation and Problem statement	4
1.3 Objectives	5
1.4 Scope of this study	5
CHAPTER 2 LITERATURE REVIEW	
2.1 Spent Mushroom Substrate (SMS)	6
2.2 Activated Carbon (AC)	8
2.3 Pyrolysis process	11
2.4 Activation Process	11
2.4.1 Chemical Activation	12
2.4.2 Physical Activation	12
2.5 Sulfide	13
2.5.1 Fundamental of sulfide	13
2.5.2 Effect of sulfide on human health	14
CHAPTER 3 MATERIAL AND METHODOLOGY	
3.1 Material and Equipment	16
3.2 Methodology	17

3.2.1	Preparation of SMS	18
3.2.2	Analysis using TGA	18
3.2.3	Pyrolysis Process	18
3.2.4	Activation of Chars	19
3.3	Characterization process	
3.3.1	Surface Area Analyzer (BET)	19
3.3.2	Scanning electron microscope (SEM)	19
3.3.3	Fourier Transform Infrared Spectrometry (FTIR)	19
3.4	Sulfide Solution Preparation	20
CHAPTER 4 RESULTS AND DISCUSSION		
4.1	Thermogravimetric Analyzer (TGA) Analysis	21
4.2	Optimization using Design Expert 7	22
4.3	Sulfide Removal	23
4.4	Characterization of Optimize AC	
4.4.1	Scanning electron microscopy (SEM)	29
4.4.2	Fourier transform infrared (FTIR)	30
4.4.3	Surface area analysis (BET)	31
CHAPTER 5 CONCLUSION		32
REFERENCES		33
APPENDICES		37

LIST OF FIGURES

Figure 1.2: World mushroom production in 2014	3
Figure 2.1: Mushroom substrate use in Mushroom Industry	7
Figure 2.2: The Shape of different types of Activated Carbon	9
Figure 3.2: Process flow chart of the experiment	16
Figure 4.1: TGA Analysis of SMS from 30 oC to 1000 oC	20
Figure 4.2: The Optimization Table generated by Design Expert 7	21
Figure 4.3.1: Percentage of sulfide removal	22
Figure 4.3.2: Graph of predicted vs actual data	25
Figure 4.3.3: Graph of normal plot of residuals	25
Figure 4.3.4: Graph of temperature vs sulfide removal	26
Figure 4.3.5: Contour plot of the data	27
Figure 4.3.6: 3D Surface plot of the data	27
Figure 4.4.1.1: Magnification 3000x	29
Figure 4.4.1.2: Magnification 5000x	29
Figure 4.4.2: FTIR spectra of activated carbon	30
Figure 4.4.3: N ₂ adsorption/desorption isotherms of AC	31

LIST OF TABLES

Table 2.1.1: .Cultivated mushrooms in Malaysia, 2014	5
Table 2.1.2: Agriculture residues as a mushroom growing medium	6
Table 2.2: Types of Activated Carbon	9
Table 2.4: Pores classification	10
Table 2.5: Acute symptom of sulfide on human health	13
Table 4.3: Analysis of variance table	23
Table 4.4.2: Infrared Band Assignments for the Chars	30

LIST OF ABBREVIATIONS

SMS	Spent mushroom substrate
AC	Activated carbon
SEM	Scanning electron microscope
BET	Surface area analyser
TGA	Thermogravimetric analyser
FTIR	Fourier transform infrared spectroscopy
SME	Small and medium sized enterprise
PhA	Physical activation
ChA	Chemical activation

CHAPTER 01

INTRODUCTION

1.1 Background

Small and Medium Enterprises (SMEs) in Malaysia has been the forefront of local economic development, even before the independence in 1957. Currently, the most recent data indicates that SMEs now account for more than 90% of all the establishments in the manufacturing, services and agricultural sector, providing around 65 % of total employment and it is expected that the value added production of SMEs to be around RM120 billion or 50 % of total production in the manufacturing sector by 2020 (Predeeban, 2013).

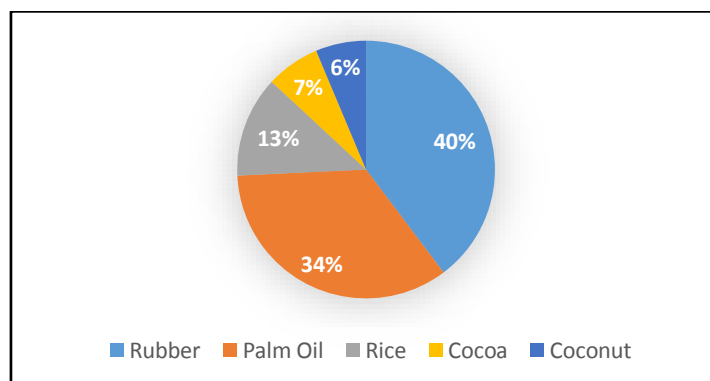


Figure 1.1: Agriculture crops grown in Malaysia in 2014

In Malaysia, the major agricultural crops grown are rubber (39.67%), palm oil (34.56%), rice (12.68%), cocoa (6.75%), and coconut (6.34%) as shown in Figure 1.1. Thus, it produces large amounts of agricultural residues, but, these waste are not always being utilizing for any further downstream operations. In Malaysia only 27.0% of agricultural wastes are used as fuel in timber industry or manufacturing industry and the rest has to be disposed of by burning (Rosmiza et al., 2016).

One of the growing agricultural industry in Malaysia today is the mushroom industry due to the high demand from all over the country. With the increasing production of mushroom, massive amount of unused and unutilized mushroom waste produced has become a huge concern for mushroom grower. Since the information on the use of mushroom waste especially the SMS as AC is still scarce in Malaysia, thus this study was deemed necessary. AC can be prepared from a vast variety of carbon-containing feedstocks by the activation of pyrolysis char either physical or chemical activation. The most common feedstocks for the commercial production of AC are anthracite and bituminous coal, lignite, peat, and the lignocellulosic wood and coconut shells (Pollard et al., 1992).

AC can be described as a highly microporous carbons which, after carbonization and activation process of the precursor material, and comprised of microcrystalline graphite layers interspersed with non-graphitic aromatic carbon structures containing heteroatoms, such as oxygen and hydrogen, and in which many carbon-carbon bonds are left incomplete, thus creating chemically active sites that are responsible for specific physical or chemical interactions with an assortment of sorbates of great relevance in adsorption processes (Oliveira L. S. and Franca A. S., 2008). In layman terms, AC can be described as thermally produced solid carbons with high porosity and high internal surface areas for high adsorption capacity.

Agricultural by-products have proven to be promising raw materials for the AC production because of their availability at a low price and compose of high carbon content. AC is a versatile product and is vastly used in different applications, such as adsorbents for waste removal and pollution control, water purification, dispersion of catalyst and catalyst support, electrochemical systems in batteries and supercapacitors, catalyst for oxygen reduction reaction in alkaline electrolyte, hydrogen storage, in food and beverage as well as steel industries. (Kaouah et al., 2013; Liu et al., 2012; Ioannidou and Zabaniotou, 2007)

In wastewater, the presence of sulfide is due to the result of biological, physical and chemical processes which mostly occurs in the submerged portion of the sewage collection networks in any chemical or industrial plant. The rate of sulfide generation depends on several factors such as pH, temperature, concentration of organic materials and nutrients, sulfate concentrations, collection system parameters and performance, and also the oxidation reduction potential. Dissolved sulfide can affect biological processes in wastewater treatment plants. Other problems by hydrogen sulfide emission were corrosion of sewer concrete pipes, release of obnoxious odors to the atmosphere, toxicity to sewer workers or human health, water supply and environment pollution, and economic effects.

In this research, the objective to remove the sulfide content that present in the petrochemical process plant sewage act as the performance measurement in order to determine the most optimize AC produce from the different conditions of AC production parameters.

1.2 Motivation and Problem statement

Nowadays, small and medium sized enterprises (SME) in Malaysia has becoming increasingly prominent because they can provide an economic growth especially in rural area for poor citizen. SME can be established in any locality for any kind of business activity and according to Wasim (2014), there are two main reasons for the existence of small firms, that are first is to provide goods or services to satisfy their customers' needs in manner that they will continue to use and recommend the firms, and secondly is to create desired goods or services so that the investment in the firm is converted to cash as quickly as possible (Wasim & Khalique, 2009).

Currently in Malaysia, mushroom industry is one of the SME that is still new and small however it's growing steadily due to the high demand of mushroom all over the globe. This is because the global mushroom trade has shown a significant increasing trend over the last three decades. The demand of mushroom for Malaysian was about 50t/day but the current production is only 24t/day (Rosmiza et al., 2016). This shows that mushroom industry have high potential to grow and expand in the near future. Figure 1.2 shows that Asian countries produce 76.64% of world mushroom markets and about 40% of total world mushroom are exported from China which make it the biggest mushroom producer in the world.

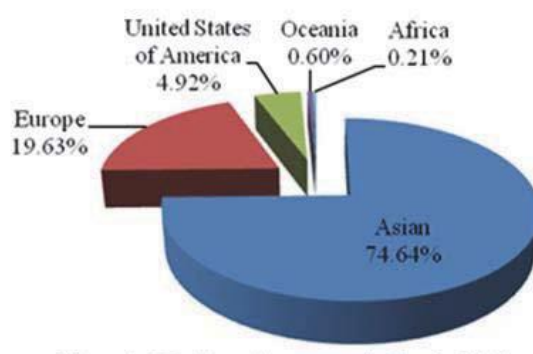


Figure 1.2: World mushroom production in 2014

Source: Food and Agriculture Organization, 2015

Despite of the large production of mushroom, the mushroom industry also produce enormous amount of waste such as the spent mushroom substrate (SMS). In the area where there are many mushroom farms are located, the disposal of SMS is a big problems for the mushroom's grower. Typically, biomass waste is landfilled or incinerated, which may lead to disposal cost and contributes to land and air pollution. Thus, this study was conducted to investigate the requirements for using these SMS for AC production that later on can be use in industrial waste water treatment such as petrochemical industry.

1.3 Objectives

Based on the research background and problem statements described in the previous section, the objectives of this research is:

- To produce AC from the SMS by using the pyrolysis method and chemical activation
- To determine the optimize condition of AC production
- To study the effects of operating parameter changes during pyrolysis in the AC produce
- To characterize the AC produce

1.4 Scopes of study

The following scopes have been identified in order to achieve the objectives:

- i. Collection of SMS sample from the Rozeriya Enterprise, Kuala Krai, Kelantan
- ii. Production of the AC using the Pyrolysis Method and Chemical Activation
- iii. Optimization of AC production using Design Expert 7
- iv. Effects of the operating parameter changes in the Pyrolysis procedures (Temperature and Time)
- v. Sulfide removal percentage of each AC produce
- vi. Characterization of AC produce using the BET Equation, SEM, FTIR and TGA

CHAPTER 02

LITERATURE REVIEW

2.1 Spent Mushroom Substrate (SMS)

Mushrooms are categorized as one of the seven high-value crops that are cultivated intensively and widely in Malaysia (<http://www.moa.gov.my>, 2011). It is considered, to be a new and small industry but it is reported steadily growing (Mohd Zaffrie et al., 2014). There are over 300 mushrooms that are edible in the world, but in Malaysia only about 17 main types have been cultivated, however only eight are now cultivated commercially as in Table 2.1.1. The most popular cultivated and easiest to market for household consumption is the Grey oyster, while Shiitake and Button mushroom are grown for the hotel trade and caterers (Rosmiza et al., 2016).

Table 2.1.1: .Cultivated mushrooms in Malaysia, 2014

<u>Mushrooms type</u>	<u>Total cultivated (%)</u>
Grey oyster (<i>Pleurotus pulmonarius</i>)	90.89%
Ling Zhi (<i>Ganoderma</i> sp.)	1.64%
King oyster (<i>Pleurotus eryngii</i>)	1.17%
Black Jelly (<i>Auricularia</i> sp.)	1.17%
Enoki/ Golden needle (<i>Flammulina velutipes</i>)	0.70%
White oyster (<i>Pleurotus florida</i>)	0.70%
Button (<i>Agaricus</i> sp.)	0.70%
Shiitake (<i>Lentinus endodes</i>)	0.70%
Paddy straw (<i>Volvariella volvaceae</i>)	0.47%
Abalon (<i>Pleurotus cystidiosus</i>)	0.23%
Chestnut (<i>Agrocybe</i> sp.)	0.23%
Red oyster (<i>Pleurotus flabellatus</i>)	0.23%
Yellow oyster (<i>Pleurotus citronipileatus</i>)	0.23%
Fungus (<i>Schizophyllum</i> sp.)	0.23%
Shaggy mane (<i>Coprinus</i> sp.)	0.23%
Monkey head (<i>Hericium erinaceum</i>)	0.23%
<u>Morning glory (<i>Citocybe</i> sp.)</u>	<u>0.23%</u>

Source: Department of Agriculture Malaysia, 2015

Different mushrooms have different growing systems. The important condition for mushrooms cultivation is where the environment need to be carefully controlled with right temperature, humidity and light. In order to increase yield, appropriate bed methods; quality of spawn; suitable substrate, and a favorable season for cultivation are particularly important. Spawn culture is highly technical and requires specialized facilities and equipment. Typical mushroom substrates which could be used including sawdust, straw of any grain crops (wheat, rice, barley and rye), logs, corn cobs, bagasse, chaff, water lily, banana leaves, cocoa bean shell, cotton straw and other agricultural by-products (Rosmiza et al., 2016). Currently in Malaysia sawdust is used as a substrate for mushroom cultivation. Through appropriate biotechnology, agriculture waste material can potentially be used as a growing medium for mushroom cultivation as shown in Table 2.1.2.

Table 2.1.2: Agriculture residues as a mushroom growing medium

Growing medium	Mushroom variety
Rice straw	Paddy straw (<i>Volvariella volvaceae</i>), Oyster (<i>Pleurotus ostreatus</i>), Button (<i>Agaricus bisporus</i>)
Sawdust-straw	Oyster, Roundhead
Sawdust-rice bran	Ear (<i>Auricularia auricular-judae</i>), Shaggy mane (<i>Coprinus sp.</i>), Shiitake (<i>Lentinus endodes</i>), Nameko (<i>Pholiota nameko</i>), Enoki (<i>Flammulina velutipes</i>)
Oil palm	Paddy straw
Cocoa shell	Oyster
Banana leaves	Paddy Straw
Coffee pulp	Oyster, Shiitake

Source: Rosmiza et al., 2016

One of the by-products in the mushroom industry in Malaysia and worldwide today is the spent mushroom substrate (SMS), also known as spent mushroom waste or spent mushroom compost. In mushroom cultivation, mushroom substrate is used as a growing medium or the growth media that act like a soil for the production of mushroom. As shown in Table 2.1.2 different growing medium are suitable for different type of mushroom.

The productivity of the mushroom substrate decreases after several cycles usually 3 - 4 times of mushroom harvesting and thus, this substrate can no longer be used and declared as spent as it has become less efficient in producing the mushroom that are suitable for marketing.

When the mushroom grows up it uses part of the compost as nutrient in producing its fruiting bodies. Most of the compost is left behind as a residue and considered as SMS. For every kilogram of mushroom cultivated, approximately 4 to 5 kg of SMS is being produced (Medina et al., 2012). The Figure 2.1 below shows the mushroom substrate use in the mushroom production company in Malaysia.



Figure 2.1: Mushroom substrate use in Mushroom Industry

2.2 Activated Carbon (AC)

Carbon compounds have been widely studied during the last century, especially after the discovery of fullerenes and carbon nanotubes, due to their versatility and various applications, such as carbon sequestration, pollutants removal, gas storage, carbon fuel cells and cell biology. Among all carbon compound, AC are probably the most broadly used class of materials. This is because of few factors including the possibility to prepare AC in different form such as powder, granular, monoliths or spherical morphology. AC also usually have a high wear resistance, good mechanical strength, good adsorption capacity and low ash content. The spherical AC have a more regular and smoother surface and a higher control over the pore size distribution (Laginhas et al., 2016).

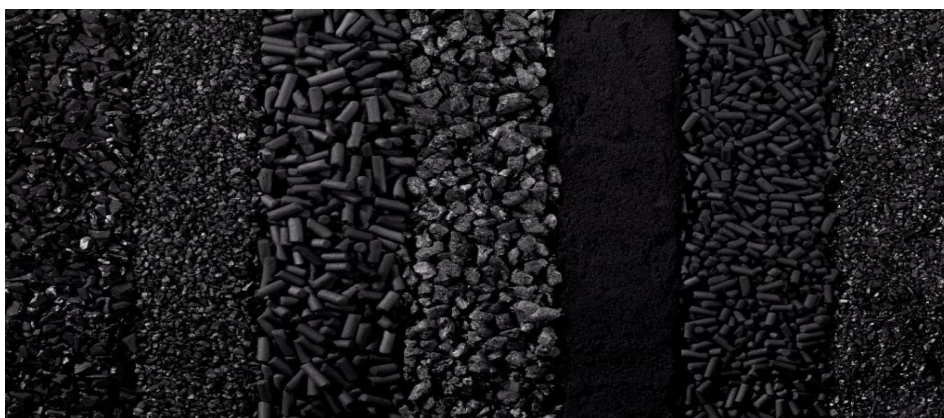
AC is a material that can be produced from charcoal or a variety of carbonaceous material (material with high carbon content) that has been treated either by physical or chemical activation after carbonization process at elevated temperature. The intrinsic properties of the activated carbon are dependent on the raw material source (carbochem.com, 2015). Activated carbon manufactured from coconut shell is considered superior to those obtained from other sources mainly because of its small macropores structure which renders it more effective for the adsorption of gas/ vapour and for the removal of colour and odour of compounds.

AC is a very effective adsorbent due to its highly developed porosity, large surface area that can reach up to 3000 m² for every gram, variable characteristics of surface chemistry, and high degree of surface reactivity (J.M. Dias et al., 2007). It has a very complex structure, with pore sizes ranging from micropores (<20 Å slit width) to macropores (>500 Å slit width), and has a variety of surface groups, impurities, and irregularities (Ismadji et al., 2005). These unique characteristics make AC very versatile materials, which have been studied not only as adsorbents, but also as catalysts and catalyst supports used for different purposes in industry such as the removal of pollutants from gaseous or liquid phases and the purification or recovery of chemicals (Derbyshire et al., 2001). Activated carbon is one of the most important microporous adsorbents from an industrial view of point. However, due to its high production costs, these materials tend to be more expensive than other adsorbents. Thus, currently there are many studies on the development of low-cost adsorbents, namely by using waste materials for that purpose. Despite the satisfactory results obtained using some of these low-cost adsorbents, AC are known to be more efficient in adsorbing a greater amount of pollutants in industry. A study shows that AC production costs can be lowered by either using a cheap raw material or by applying a proper production method (Lafi, 2001).

There are different physical forms by which AC can be found, including granulated AC, powdered AC, and extruded AC or commonly known as pelletized AC. Table 2.2 shows the types of AC, its raw material and application. While Figure 2.2 shows the pictures of the shape of different types of AC.

Table 2.2: Types of Activated Carbon

Activated Carbon Types	Raw material	Size (mm)	Application
Granular	Coconut shells	0.177	Column filter for gas/liquid treatment
Powder	Wood sawdust	<0.177	Water treatment to remove taste & odour
Extruded/Pellet	Coal base	4.000	Filtration in aquarium, ponds and pools

**Figure 2.2: The Shape of different types of Activated Carbon**

The AC derived from the waste materials has several advantages, mainly of economic and environmental nature. Recently, a wide variety of AC have been prepared from different waste materials; conventional wastes such as waste from agriculture and wood industry as well as non-conventional wastes from municipal and industrial activities have also been used.

2.3 Pyrolysis Process

Pyrolysis is a thermochemical decomposition of organic substances by heating at high temperature. Pyrolysis is a Greek-derived terminology which is ‘pyro’ means fire and ‘lysis’ mean decomposition. Pyrolysis of biomass by heat-treatment at higher temperatures generates char, oil and various gases to be used for sustainable and potential end products (Tehrani et al., 2014). Thus, agricultural residues with virtually high carbon content can be readily processed to high surface area carbons with micro and mesoporous structures either by a physical or chemical activation. It involves the simultaneous change of chemical composition and physical phase, and is irreversible. Pyrolysis is a type of thermolysis, and is most commonly observed in organic materials exposed to high temperatures. It is one of the processes involved in charring wood, starting at 200–300 °C (Zhu et al., 2016). In general, pyrolysis of organic substances produces gas and liquid products and leaves a solid residue richer in carbon content, char. Extreme pyrolysis, which leaves mostly carbon as the residue, is called carbonization. Pyrolysis differs from other processes like combustion and hydrolysis in that it usually does not involve reactions with oxygen, water, or any other reagents.

2.4 Activation Process

The activation process is crucial to determine the extent of adsorption reversibility and/or bio regeneration (Aktas & Cecen, 2007). AC texture includes a wide range of pores that can be classified according to their width as shown in Table 2.4.

Table 2.4: Pores classification

Pore type	Width of the pore (nm)
Micropores	< 2
Mesopores	2 – 50
Macropores	450

Source: (Dias et al., 2007).

In order to increase its adsorption capacity, the pore network should be developed during AC preparation by application of either adequate physical or chemical treatments.

2.4.1 Chemical Activation

Physical activation (PhA) is normally start with carbonization followed by activation using steam or CO₂; during carbonization, the material is pyrolyzed to remove non-carbon elements and formed chars, then activation occurs, at temperatures ranging from 700 to 1100 °C, using gases that open and develop the porosity of the carbonized material (Rodri'gues-Reinoso, 1997).

2.4.2 Physical Activation

Chemical activation (ChA) is a one-step method used for the preparation of AC and is the commonly used method for industrial AC production; different chemical activating agents will be used and some examples are, Zinc chloride(ZnCl₂), Phosphoric acid(H₃PO₄), Potassium hydroxide(KOH), Potassium carbonate(K₂CO₃) and Sulphuric acid(H₂SO₄). The chemical agents help to develop the AC porosity, by means of dehydration and degradation; the mixture of the chemical and the chars is then heated at a maximum of 750 °C for a certain time. The use of a lower temperature, compared to PhA, is compensated by the interaction between the chemicals and the carbon skeleton. Main advantages of ChA are the higher yield, lower temperature of activation (less energy costs), less activation time and, generally, higher development of porosity; among the disadvantages are the activating agents costs and the need to perform an additional washing stage to remove the chemical agent (Macia'-Agullo' et al., 2004). To optimize preparation procedures, the parameters normally studied are time of carbonization, temperature and CO₂/steam flow rate for PhA while time of impregnation and impregnation ratio of chemical agents for ChA. AC characteristics such as its surface area strongly depend on both the raw material and the activation procedure (Dias et al., 2007).

2.5 Sulfide

2.5.1 Fundamental of sulfide

The term sulfide refers to few types of chemical compounds containing sulfur in its lowest oxidation number of -2. Hydrogen sulfide (H₂S) is a dense, colorless, strongly odorous toxic gas that can corrodes infrastructures and impairs the performance of wastewater treatment operations.

Hydrogen sulfide is naturally converted to sulfuric acid that is corrosive towards steel and concrete. Control of H₂S will result in increased life and lower maintenance cost for facilities and piping of a processing plant. In addition, worker safety is a concern as hydrogen sulfide is extremely toxic at levels above 500 ppm, which can be reached in confined spaces.

Sulfide exists in wastewater in three forms; hydrogen sulfide gas (H₂S), non-volatile ionic species hydrogen sulfide (HS⁻) and sulfide (S₂⁻). The ratio of each of the three species H₂S, HS⁻ and S₂⁻ are dependent on the pH value. At pH 6, 90% of the sulfide will be exist as H₂S, the higher the H₂S concentration the greater the tendency for it to volatilize. Conversely at pH 10, 100% of the sulfide will be exist as S₂⁻ (Jalil E. H., 2016).

Hydrogen sulfide occurs naturally through the anaerobic decay of organic matter and is recognized by its characteristic rotten egg odour. In typical domestic wastewater, microbial reduction of the sulfate ion is the dominant mechanism for sulfide formation. In the absence of dissolved oxygen and in the presence of soluble Biological Oxygen Demand, *Desulfovibrio desulfuricans* and other sulfate-reducing bacteria that convert the sulfate ion into sulfide.



Hydrogen sulfide formation in wastewater systems occurs primarily in the gelatinous slime layer that accumulates on pipe walls and in the sludge blankets of clarifiers and other solids processing units. The rate of sulfide production is dependent upon the concentrations of sulfate ions, organic matter, and dissolved oxygen, as well as other factors such as pH, temperature, retention time, stream velocity, and surface area (Bentzen et al, 1995).

2.5 Effect of sulfide on human health

Humans may be exposed to hydrogen sulfide from endogenous production and from exogenous sources. Most endogenous production results from the metabolism of sulfhydryl-containing amino acids (e.g., cysteine) by bacteria present in both the intestinal tract and the mouth (Beauchamp et al, 1984).

Hydrogen sulfide is also produced in the brain and several smooth muscles (e.g., thoracic aorta, ileum, and portal vein) by enzymes found in these tissues (Hosoki et al, 1997). The inhalation route is the major route of exogenous intake of hydrogen sulfide. The oral route is of no practical relevance. The principal adverse health effects noted in humans exposed for short periods to high concentrations of hydrogen sulfide by inhalation include respiratory and neurological effects; death may result as a consequence of respiratory failure. Hydrogen sulfide is also an ocular and respiratory tract irritant. There is also some evidence that exposure to hydrogen sulfide may be associated with an increased rate of spontaneous abortion.

Workers are primarily exposed to hydrogen sulfide by breathing it. The effects depend on how much hydrogen sulfide ones breathe and for how long. Exposure to very high concentrations can quickly lead to death. Short-term symptoms and effects released by Occupational Safety & Health Administration of United State are shown in Table 2.5.

Table 2.5: Acute symptom of sulfide on human health

Concentration (ppm)	Symptoms/Effects
0.01-1.5	Odour threshold (when rotten egg smell is first noticeable to some). Odour becomes more offensive at 3-5 ppm. Above 30 ppm, odour described as sweet or sickeningly sweet.
2-5	Prolonged exposure may cause nausea, tearing of the eyes, headaches or loss of sleep. Airway problems (bronchial constriction) in some asthma patients.

20	Possible fatigue, loss of appetite, headache, irritability, poor memory, dizziness.
50-100	Slight conjunctivitis ("gas eye") and respiratory tract irritation after 1 hour. May cause digestive upset and loss of appetite.
100	Coughing, eye irritation, loss of smell after 2-15 minutes (olfactory fatigue). Altered breathing, drowsiness after 15-30 minutes. Throat irritation after 1 hour. Gradual increase in severity of symptoms over several hours. Death may occur after 48 hours.
100-150	Loss of smell (olfactory fatigue or paralysis).
200-300	Marked conjunctivitis and respiratory tract irritation after 1 hour. Pulmonary oedema may occur from prolonged exposure.
500-700	Staggering, collapse in 5 minutes. Serious damage to the eyes in 30 minutes. Death after 30-60 minutes.
700-1000	Rapid unconsciousness, "knockdown" or immediate collapse within 1 to 2 breaths, breathing stops, death within minutes.
1000-2000	Nearly instant death

CHAPTER 03

MATERIALS AND METHODOLOGY

3.1 Materials and Equipment

The raw material or the biomass used in this study are the spent mushroom substrate (SMS) that are taken from the Rozeriya Enterprise, a Malaysia's frozen food industry that located in Kuala Krai, Kelantan. The chemical used in the research is Potassium hydroxide (KOH), Hydrochloric acid (HCl), Sodium Sulfate (Na_2S) and Reagent 1 and 2 for sulphide analysis. While the equipment that are used during the study are the Oven, Furnace, Blender, Sieve tray shaker, Hot plate, Thermogravimetric analyser (TGA), Surface area analyser (BET), Scanning Electron Microscope (SEM) and Fourier transform infrared spectroscopy (FTIR).

3.2 Methodology

A schematic structure of the whole process flow for this study has been constructed and illustrated in the Figure 3.2.

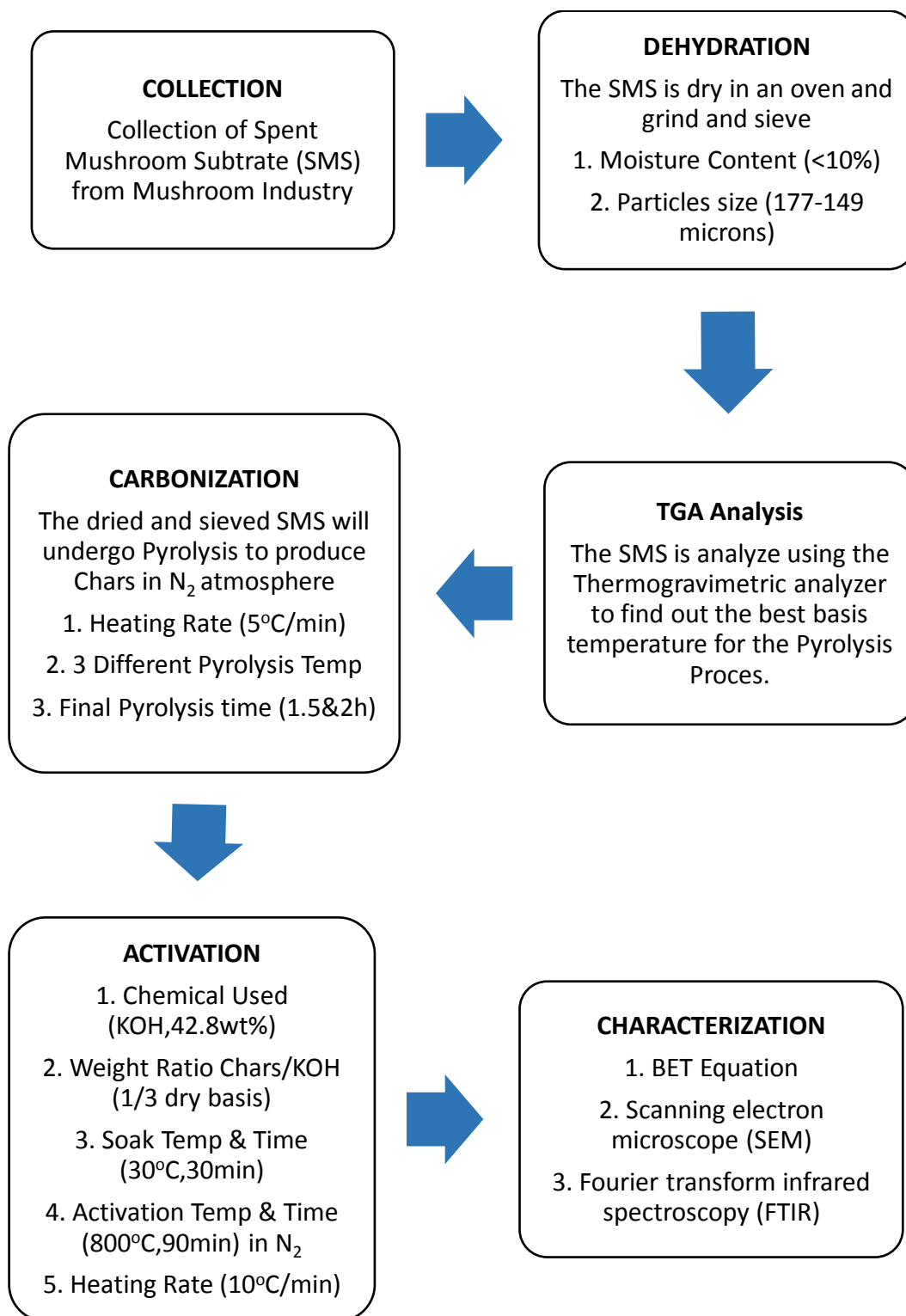


Figure 3.2: Process flow chart of the experiment

As the starting point, the SMS investigated in this study will be collected from the Rozeriya Enterprise, a frozen food industry located in Kuala Krai, Kelantan, Malaysia. Then the collected SMS are prepared for the AC production by the Pyrolysis method and Chemical activation using Potassium hydroxide, KOH. The production process of activated carbon can be divided into three major steps, first is the dehydration, followed by carbonization, and lastly the activation. Dehydration is a drying process for removal of moisture or water content from the SMS. Carbonization is the conversion of organic substance contained in the SMS into primary carbon, which is a mixture of amorphous and crystallized carbon, tar, and ash and commonly be called as chars. Activation, is the last and important step in these process, where the chars are converted into AC by the Chemical activation.

3.2.1 Preparation of SMS

The collected SMS first undergo dehydration process where the SMS is dry in an oven at 85°C for 4 h. After 4 h, the samples are weighed and recorded. These step is repeated after 10 minutes until the weight of the samples is constant that indicates the samples is totally dried. Then, the dried SMS was grinded and sieved to 250 micrometer before further use. (*Refer Appendix B for the methodology of SMS sample preparation*)

3.2.2 Analysis using TGA

The SMS then was analyzed using the Thermogravimetric Analyzer (TGA) to find the best temperature for Pyrolysis process. TGA is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature. The temperature obtain from this process is use as a basis for the final Pyrolysis temperature during Carbonization or Pyrolysis process.

3.2.3 Pyrolysis Process

This process is also known as carbonization where in a nitrogen atmospheric (99.995%) the dried, sieved and analyzed SMS was heated at a rate of 5°C/min to a final pyrolysis temperature ranging around the temperature obtain from the TGA. Then the final pyrolysis temperature was maintained for about 1.5 h to 2.0h based on the table generated by Design Expert 7. (*Refer Appendix A for the methodology of carbonization and activation*)

3.2.4 Activation of Chars

The chars produced was soaked with KOH solution (42.8 wt.%) with a Chars/KOH weight ratio of 1/3 on a dry basis. The mixture was kept at 30°C for 30 min in an oven. Then, the mixture was filtered and the solid obtain was dry in an oven. The dried solid was then heated to 800°C for 90 min in a nitrogen (99.995%) purged tube furnace with a heating rate of 10°C/min. The AC obtained was cooled under the nitrogen flow then washed with 1 M Hydrochloric acid, HCl before it was washed with deionized water until the pH of the filtrate became constant. (*Refer Appendix A for the methodology of carbonization and activation*)

3.3 Characterization of AC

3.3.1 Surface area analyser (BET Equation)

The BET surface area method to measure the total internal surface area and average pore diameter of AC produce. The mathematical model uses the nitrogen adsorption isotherm at low temperature and single layer adsorption.

3.3.2 Scanning electron microscope (SEM)

SEM is use to analyze the morphology of the AC produce as it can generate the images of the sample by scanning it with a focuses beam of electron that interact with the sample's atom to obtain the information of the sample's surface topography and composition.

3.3.3 Fourier transform infrared spectroscopy (FTIR)

FTIR is use to investigate the possible chemical functional group in the sample. It is a technique use to obtain infrared spectrum of absorption or emission of a solid, liquid or gas.

3.4 Sulfide Solution Preparation

For preparation of the sulfide solution by considering the degradation of the sulfide, 0.35g of sodium sulfide flake was diluted in a 1000 mL deionized water to make ± 30 mg/L of sulfide content. In order to get the reading, dilution has been done as the DR 2800 spectrophotometer limit was only 800 $\mu\text{g/L}$ of sulfide content that was readable. The 50 times dilution was chosen where 2 ml of synthetic wastewater was mixed with 100 ml of deionized water. (*Refer Appendix C for the methodology of sulfide solution preparation*)

While for the sulfide removal testing, 20ml of the measured sulfide content diluted sulfide solution was measured and put in a 50 ml beaker. A stirrer was added and set at 500 rpm. Then, the AC was added to the solution for 3 minutes and the final solution sulfide was then measured again. (*Refer Appendix D for the methodology of sulfide removal*)

The percentage of sulfide removal was calculated using the equation 1:

$$\% \text{ removal} = \frac{30 - 0.4}{30} \times 100 \quad \text{equation 1}$$

CHAPTER 04

RESULTS AND DISCUSSION

4.1 Thermogravimetric Analyzer (TGA) Analysis

The SMS was then sent to FIST's laboratory to be analyzed by the TGA to find out the best temperature range for Pyrolysis process in this research. The result from the TGA analysis as shown in Figure 4.1 was analyze and the temperature range was decided from 300 °C to 700 °C.

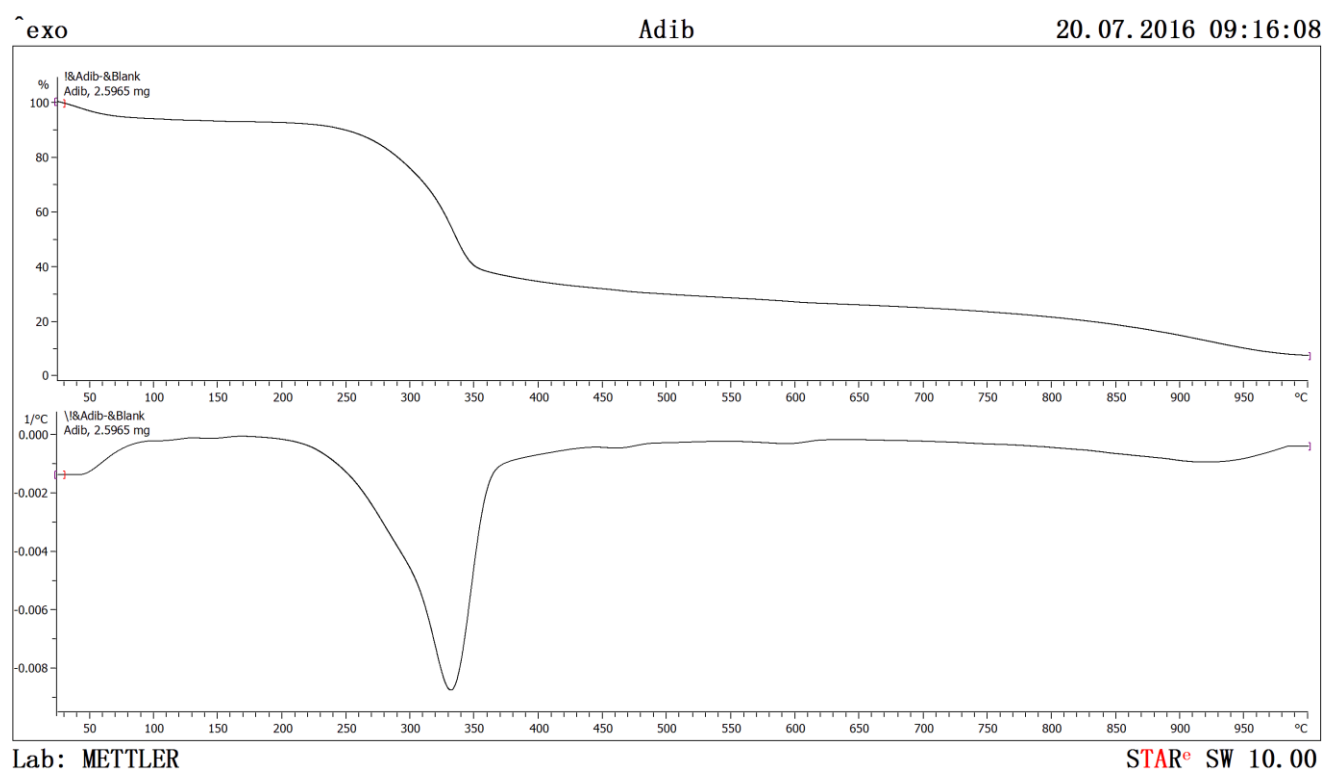


Figure 4.1: TGA Analysis of SMS from 30 °C to 1000 °C

Thermogravimetric Analysis (TGA) has been performed in order to identify the weight loss with increasing temperature of the SMS.

The TG and DTG curves of the SMS are shown on Figure 1. The weight loss before 100 °C was attributed to the loss of adsorbed water content in the SMS; the weight loss between 120 to 200 °C may have been due to the decomposition of small organic molecules in the SMS, such as amino acids and fatty acids that generated by the cultivation process during mushroom production; the most significant weight loss, between 250 and 350 °C, was mainly due to the

pyrolysis of hemicellulose and cellulose in the SMS; the weight loss between 440 and 480 °C indicated the decomposition of CaC_2O_4 into CaCO_3 and CO ; the peak between 570 and 610 °C was attributed to the decomposition of CaCO_3 into CaO and CO_2 .

4.2 Optimization using Design Expert 7

An engineering approach such as Optimization has been used in this study. Design Expert 7.0 software was used for the Optimization in order to find the best operating condition in AC production. The factors of heating time (hours) and heating temperature (°C) was being studied and the response recorded is the sulphide removal (%). The Table generated by the Design Expert 7 is shown in Figure 4.2.

Select	Std	Run	Factor 1 A:Heating Tem °C	Factor 2 B:Heating Time min	Response 1 Sulfide Remov mg/l
	1	4	400.00	97.50	
	2	2	600.00	97.50	
	3	7	400.00	112.50	
	4	10	600.00	112.50	
	5	8	300.00	105.00	
	6	5	700.00	105.00	
	7	3	500.00	90.00	
	8	12	500.00	120.00	
	9	11	500.00	105.00	
	10	6	500.00	105.00	
	11	1	500.00	105.00	
	12	13	500.00	105.00	
	13	9	500.00	105.00	

Figure 4.2: The Optimization Table generated by Design Expert 7

4.3 Sulfide Removal

The results obtained for sulfide removal percentage from 3 minutes residence time and at room temperature was shown in Figure 4.3.1.

Select	Std	Run	Factor 1 A:Temp °C	Factor 2 B:Time min	Response 1 Sulfide Remov %
	1	1	400.00	97.50	62.67
	2	12	600.00	97.50	78.57
	3	9	400.00	112.50	74.68
	4	2	600.00	112.50	73.35
	5	10	300.00	105.00	46.61
	6	5	700.00	105.00	61.06
	7	3	500.00	90.00	86.1
	8	6	500.00	120.00	89.09
	9	11	500.00	105.00	91.1
	10	7	500.00	105.00	92.64
	11	13	500.00	105.00	93.15
	12	4	500.00	105.00	93.15
	13	8	500.00	105.00	93.4

Figure 4.3.1: Percentage of sulfide removal

In order to determine the optimum condition of activated carbon production, 2 parameter are being studied that is the temperature of pyrolysis process and the time of pyrolysis process. The experimental set up and corresponding experimental response are shown in Figure 4.3.1. The lowest sulfide removal percentage value of 46.61% was obtained at temperature 300°C and time of 105 minutes; while the highest sulfide removal percent value of 93.40% was obtained at temperature 500°C and time of 105 minutes.

Fitting of the data to various models (linear, two factorial, quadratic and cubic) and their subsequent analysis of variance showed that the sulfide removal of activated carbons produce are most properly described by the quadratic polynomial model.

The adjusted R^2 of the quadratic model (0.8463) was the highest. The cubic model was found to be aliased. The second-order polynomial model used to express the sulfide removal percentage of activated carbon produce as a function of independent variables are as shown in the Equation 1 and Equation 2 in term of coded and actual levels.

$$\text{Sulfide Removal (coded)} = 90.10 + 3.62A + 1.06B - 4.31AB - 9.88A^2 - 1.44B^2$$

Equation 1

$$\text{Sulfide Removal (actual)} = -772.58105 + 1.62678A + 8.37105B - 5.74333 \times 10^{-3}AB - 9.87504 \times 10^{-4}A^2 - 0.025512B^2$$

Equation 2

The analysis of variance table extracted from the Design Expert software has been shown in the Table 4.3 below

Table 4.3: Analysis of variance table

Source	Sum of Squares	dF	Mean Square	F Value	p-value Prob > F
Model	2526.44	5	505.29	14.22	0.0015 ^a
A – Temp	157.47	1	157.47	4.43	0.0733
B – Time	13.59	1	13.59	0.38	0.5559
AB	74.22	1	74.22	2.09	0.1917
A ²	2234.45	1	2234.45	62.87	<0.0001
B ²	47.19	1	47.19	1.33	0.2870
Residual	248.79	7	35.54		
Lack of Fit	245.33	3	81.78	94.60	0.0004 ^a
Pure Error	3.46	4	0.86		
Cor Total	2775.23	12			
R ²	0.9104				
Adj. R ²	0.8463				

^a Significant

Table 4.3 summarizes the ANOVA (F-test) and p-value that are used to estimate the coefficient of the model, to check the significant of each parameter, and to indicate the interaction strength of each parameter. It was observed from the ANOVA analysis that the confidence level was around 95% while the p-value of the model was less than 0.0004.

The model with the p-value less than 0.05 was statistically significant, which implied that the model was suitable for this experiment. The "Lack of Fit F-value" of 94.60 implies the Lack of Fit is significant. There is only a 0.04% chance that a "Lack of Fit F-value" this large could occur due to noise. Significant lack of fit was bad; we want the model to fit.

The "Pred R²" of 0.3927 is not as close to the "Adj R²" of 0.846397 as one might normally expect. This may indicate a large block effect or a possible problem with the model and/or data. Things to consider are model reduction, response transformation, outliers, etc. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 11.542 indicates an adequate signal. This model can be used to navigate the design space

The coefficient of determination (R²) and adjusted coefficient of determination (R²adj) were 0.9104 and 0.8463, respectively which indicates that the estimated model fits the experimental data satisfactorily. Lee et al. (2010) suggested that for a good fit of a model, R² should be at least 0.80. The R² for these response variables was higher than 0.80, indicating that the regression models explained the mechanism well.

In the Figure 4.3.2 below showed the result of the actual versus predicted data while Figure 4.3.3 showed the normal plot of residuals.

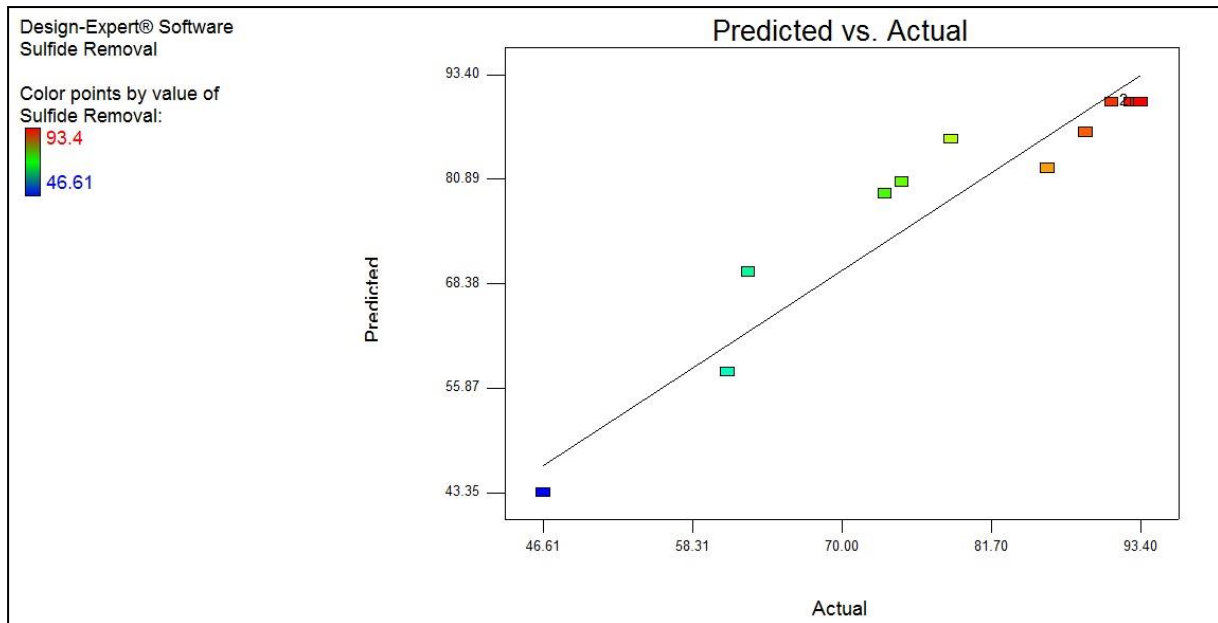


Figure 4.3.2: Graph of predicted vs actual data

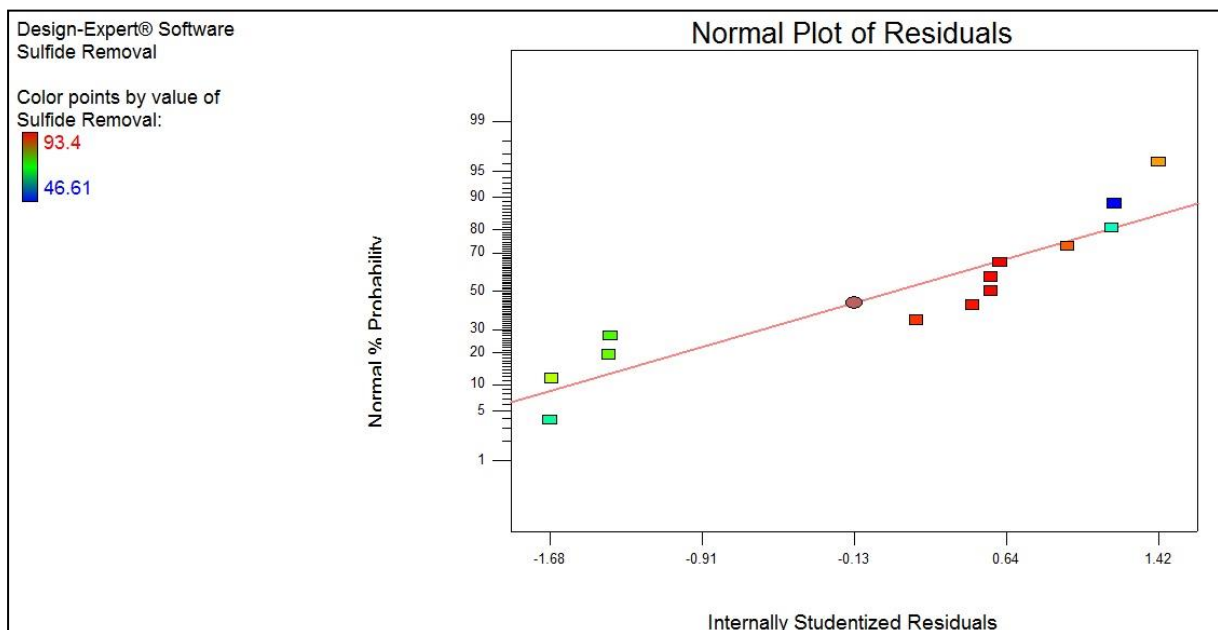


Figure 4.3.3: Graph of normal plot of residuals

A linear distribution is observed which is indicative of a well-fitting model. The values predicted were close to the observed values of sulfide removal. The plot indicates that the difference between actual and predicted values follow a normal distribution and form an approximately straight line.

From Table 4.3, the p-value of factor A (temperature) is smaller than factor B (time) which is 0.0733 and 0.5559 respectively. These values proved that temperature was the main factor that effects the sulfide removal. The effect of temperature to sulfide removal was shown as in Figure 4.3.4. While the contour plot and 3D surface plot of the data were showed in the Figure 4.3.5 and Figure 4.3.6 respectively.

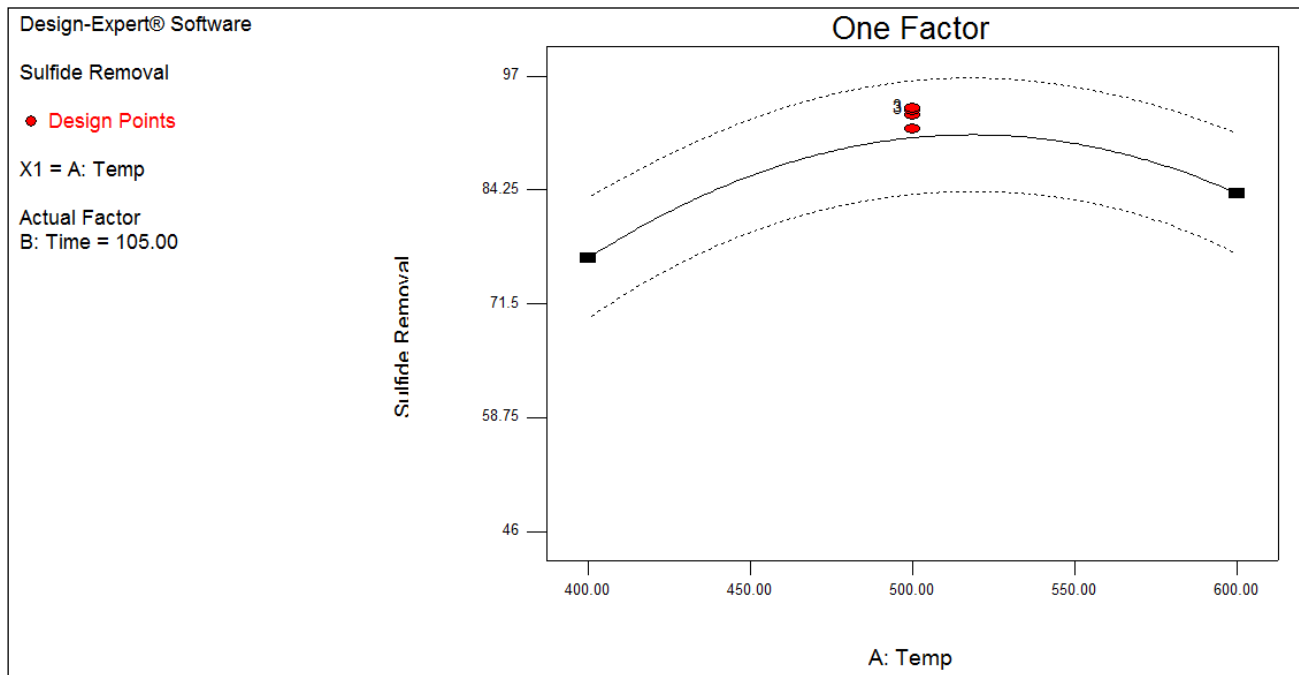


Figure 4.3.4: Graph of temperature vs sulfide removal

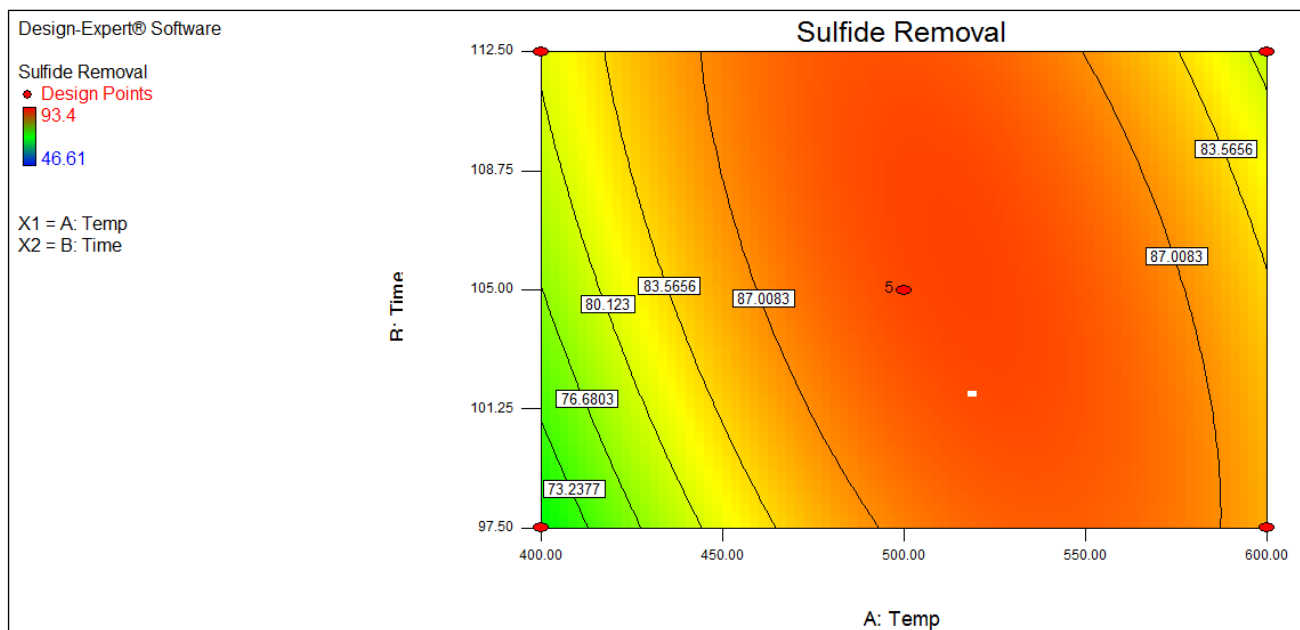


Figure 4.3.5: Contour plot of the data

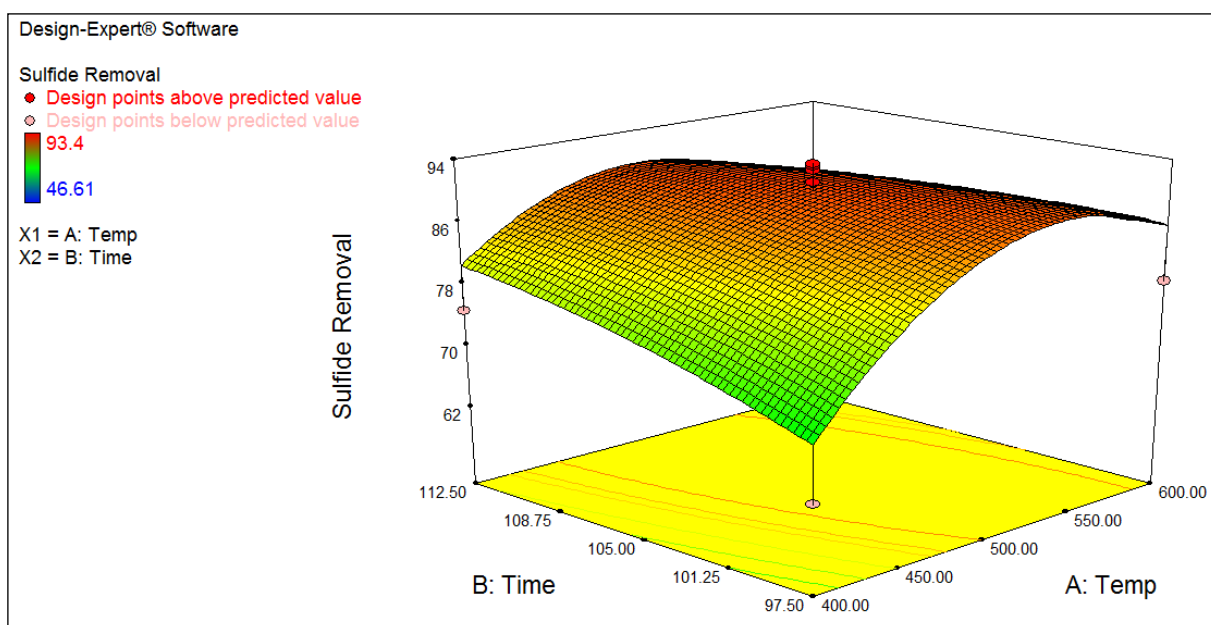


Figure 4.3.6: 3D Surface plot of the data

The effects of interaction between factors, i.e. temperature, time and sulfide removal are shown in Figure 4.3.5 and Figure 4.3.6.

The plotted data depicts the effects of temperature and heating time on the sulfide removal highest at 93.4%. The effect of sulfide removal is more significant effected by the change of temperature as shown in Figure 4.3.4. The effect may be attributed to the number and size of pores during heating. Which at optimum conditions the reaction is higher and tend to produce a better performance activated carbon.

4.4 Characterization of Optimize AC

4.4.1 Scanning electron microscopy (SEM)

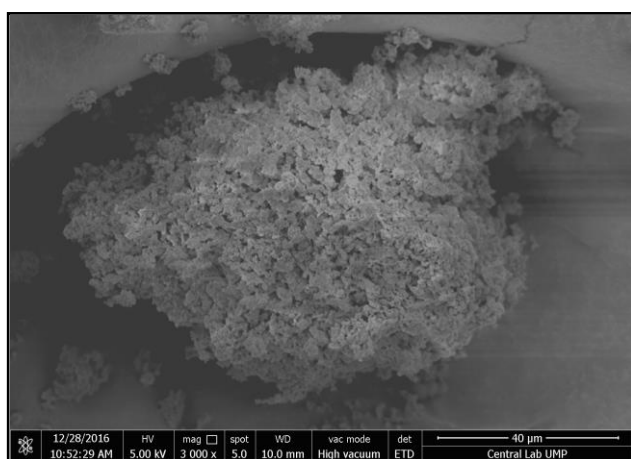


Figure 4.4.1.1: Magnification 3000x

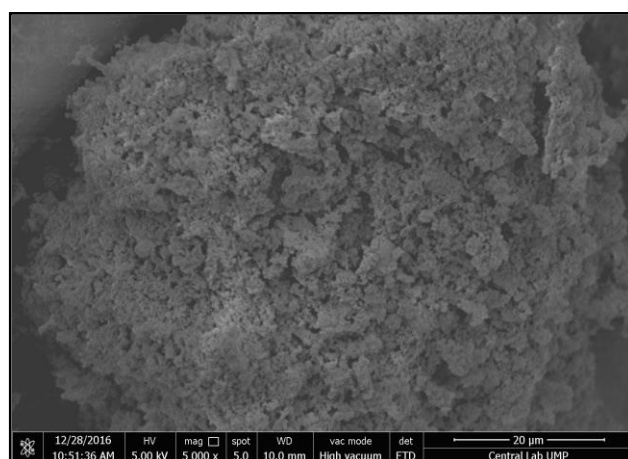


Figure 4.4.1.2: Magnification 5000x

Figure 4.4.1.1 and 4.4.1.2 show the SEM images of the optimize AC produce at the temperature of 515°C. Different pyrolysis temperature can caused substantial changes to the surface morphology of the AC. From these figures, the AC had a rough surface with many pores and deep crack due to the dramatic release of different volatile compounds occurred as the temperature increased, leading to the formation of its loose structure.

4.4.2 Fourier transform infrared (FTIR)

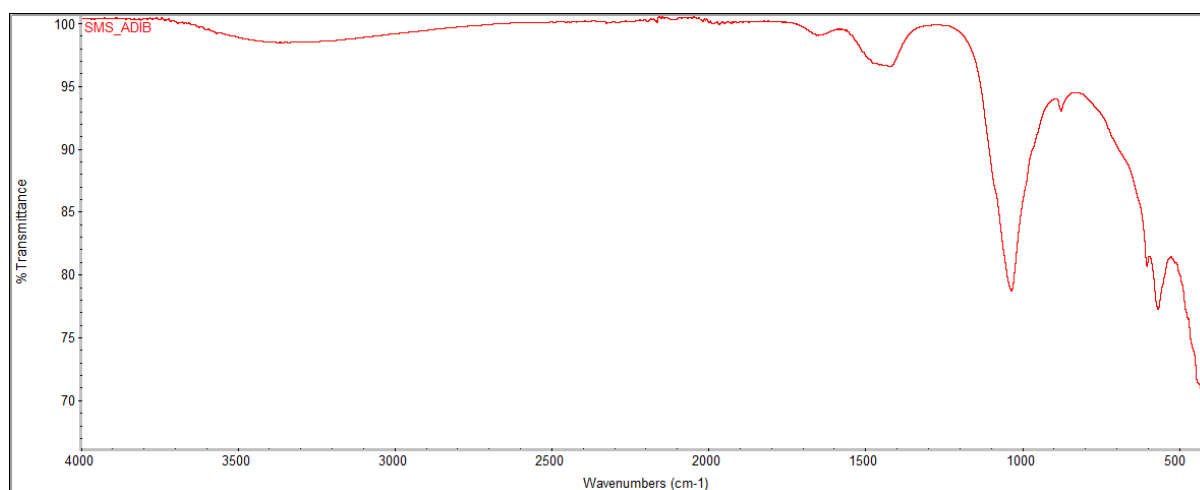


Figure 4.4.2: FTIR spectra of activated carbon

FTIR spectra for the activated carbon obtained is as shown in Figure 4.4.2. The functional groups identified from the FTIR are given in Table 4.4.2. Small peak at around 3400 cm^{-1} indicating the complete volatilization of oxygen-containing groups due to the high pyrolysis temperature. While an absorption peak at 1600 cm^{-1} indicating the presence of polynuclear aromatic compounds. However the intensity of peak is small. The absorption peaks at 1400 and 850 cm^{-1} , representing aromatic C-H vibration, the intensity of the absorption peak at 1050 cm^{-1} is the highest, which was attributed to C-O stretching. Since SMS has high oxygen content, this phenomenon can be explained by the possibility that the intense interaction between oxygen and carbon during pyrolysis led to the firm combination.

Table 4.4.2: Infrared Band Assignments for the Chars

Wavenumber (cm^{-1})	Description
3420	-OH stretching in phenols and alcohols
2925	Aliphatic CH_3 stretching in alkanes
2850	Aliphatic CH_2 stretching in alkanes
2360	C=O asymmetric stretching vibration of CO_2
1635	C=O stretching (acid, aldehyde and ketone)
1590	In-plane skeletal vibrations in aromatic rings
1416	Aromatic C-H vibration
1315	In-plane bending vibration of phenolic -OH
1049	C-O (anhydrides) stretching
873	Out-plane bending vibration of aromatic C-H

4.4.3 Surface area analysis (BET)

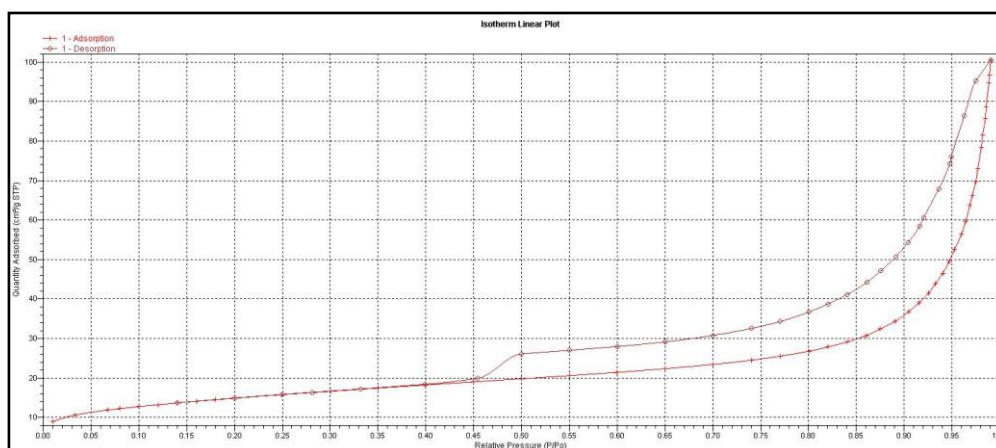


Figure 4.4.3: N₂ adsorption/desorption isotherms of AC

The N₂ adsorption/desorption isotherms are shown in Figure 4.4.3. The optimize AC shows isotherms similar to Type I-B as defined by IUPAC, indicating the presence of a complex micropore structure. Moreover, they contained no distinct plateaus even at high relative pressure because some mesopores resulted in a more enhancement near saturation. At higher relative pressure, the hysteresis loop (Type H₄) is indicative of slit-shaped pores. The BET surface area and total pore volume of optimize AC were 51.7755 m²/g and 0.002537 cm³/g respectively.

CHAPTER 05

CONCLUSION

From this research, it can be concluded that higher sulfide removal can be achieved in the optimum condition at the heating temperature around 515°C and heating time around 106 minutes with the sulfide removal at 93.7%. The final sulfide removal percentage of the activated carbon produced was achieved based on the optimization analysis and validation of experiment that was run three times in order to ensure the results obtain by using the Design Expert 7 and experimental does not deviate. The error obtain from experimental is less than 4% as compare with the one obtain from Design Expert 7. Thus, the objective of this research project was successfully achieved. The BET surface area and total pore volume of optimize AC were 51.7755 m²/g and 0.002537 cm³/g respectively. These prove that AC derived from agriculture waste especially from mushroom industry waste also have high potential to be used as petrochemical plant's wastewater treatment.

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APPENDICES

Appendix A: Carbonization and Activation Procedure



Weighing of the dried
& sieved SMS



Carbonization of SMS
at high temperature



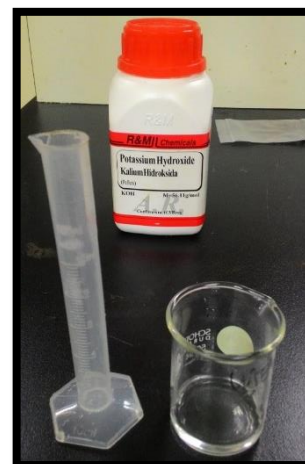
The chars obtained
after carbonization



Final AC



Impregnation the Chars
with KOH solution

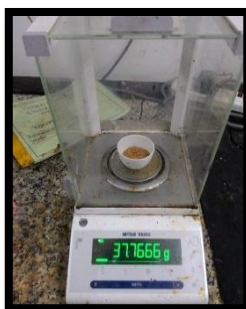


Chemical activation
by KOH

Appendix B: SMS Sample Preparation Procedure



The SMS sample was placed in a crucible dish



The SMS and crucible was weighed



The SMS was placed in an Oven for 4h at 85 °C



The dried and sieved SMS was stored in a plastic seal bag



Then the SMS was sieved to 250 μm



The dried SMS is then blended using blender

Appendix C: Sulfide Solution Preparation Procedure



0.5g of Na_2S was weighed



Dilute the Na_2S in 1L volumetric flask

Appendix D: Sulfide Removal Procedure



0.5g of AC produced was weight



25ml of sulphide solution was prepared



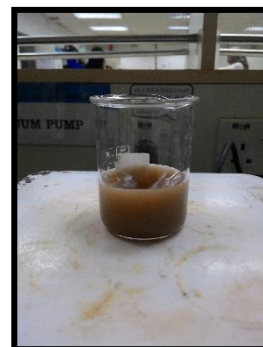
0.5g was mixed with sulphide solution for 3 min at constant stirring rate



Reagent 1 & 2 was mix with the sample for sulphide testing



The sample was then filtered in a vial



The mix was left for 3 min for the reaction to occur



Then put the sample to read the sulphide content in it