SULFUR DIOXIDE REMOVAL USING DRIED EGGSHELL

HOO SIE KEI

A project report submitted in partial fulfilment of the requirements for the award of the degree of Bachelor of Engineering (Hons.) Environmental Engineering

Faculty of Engineering and Green Technology
Universiti Tunku Abdul Rahman

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DECLARATION

I hereby declare this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"SULFUR DIOXIDE REMOVAL USING DRIED EGGSHELL"** was prepared by **HOO SIE KEI** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Environmental Engineering at Universiti Tunku Abdul Rahman.

Approved by,

Signature : ______________________

Supervisor : Dr. Sumathi a/p Sethupathi

Date : ______________________

Specially dedicated to my beloved father and mother.
“Thank you for loving me all the times, and give me supports whenever I need them!
Love you forever.”

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ABSTRACT

Due to the global industrialization, the emission of sulfur dioxide gas becomes a concern nowadays. SO_2 has adverse effects to the environment as it tends to react with water to form acid rain. The interests of turning eggshell waste to products had been growing in different sectors. However, only a few research had been done using eggshell waste for gas removal. In this study, eggshell-based adsorbents (with membrane and without membrane) were prepared without undergoing any modifications. The adsorption test using eggshell-based adsorbents were carried out at three different parameters, where the influence of particle size, reactor temperature and relative humidity were studied and evaluated. Owning to the presence of a network of fibrous protein offers large surface area to eggshell with membrane (ESM), it showed better adsorption capacity than the eggshell without membrane (ES). Besides, comparison had been done between commercial calcium carbonate (CCC) and ESM, where the results showed CCC had higher SO_2 removal capacity, where the purity grade of CCC, which is approximately 99% was believed as one of the main reason to have better adsorption performance. At the presence of 40% relative humidity, significant breakthrough time had observed in ESM and CCC, where the adsorption capacity were 18.7472 SO_2 mg/g and 23.2435 SO_2 mg/g. The adsorbed water to the adsorbents enhanced the ion mobility, permit SO_2 hydrolysis reaction to produce H_2SO_3. Characterizations of the eggshell-based adsorbents had been evaluated by FTIR, SEM and EDS analysis.

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LIST OF SYMBOLS / ABBREVIATIONS

c	Outlet Concentration of Sulfur Dioxide, ppm
C_o	Initial Inlet Concentration, ppm
K_L	Langmuir Constant
M_w	Sulfur dioxide molecular weight, g/mol
q	Total Flow Rate, L/min
Q	Adsorption Capacity of Adsorbent, mg SO_2/g
R_L	Separation Factor
t	Time, min
V_m	Molar Volume, L/mol
w	Weight of Adsorbent, g
^oC	Degree Celsius
G	Giga
J	Joule
kcal	Kilocalories
m^3	Meter Cube
mg	Milligram
mm	Millimeter
ppm	Parts-per-million, 10^{-6}
µm	Micrometer
µg	Microgram
mol	Mole
ABP	Animal By-Products

C	Carbon
Ca	Calcium
$CaCO_3$	Calcium Carbonate
CaO	Calcium Oxide
$Ca(OH)_2$	Calcium Hydroxide
$CaSO_3$	Calcium Sulfite
$CaSO_4.2H_2O$	Calcium Sulfate Dihydrate (gypsum)
CCC	Commercial Calcium Carbonate
Cd	Cadmium
CH_4	Methane Gas
CO	Carbon Monoxide
CO_2	Carbon Dioxide
Cr (III)	Chromium (III)
DEA	Diethylamine
ES	Eggshell Without Membrane
ESM	Eggshell With Membrane
EU	European Union
Fe^{3+}	Ferric Cation
FGD	Flue Gas Desulphurisation
GO	Graphene Oxide
H_2	Hydrogen
H_2S	Hydrogen Sulfide
HNO_3	Nitric Acid
HO_2	Hydroperoxyl
H_2S	Hydrogen Sulfide
H_2SO_3	Sulfurous acid
K	Kelvin
kWh	Kilowatt Hour
L	Liter
mCB	Modified Carbon Black
MEA	Monoethanolamine

Mg	Magnesium
MOFs	Metal Organic Frameworks
$(NH_4)_2CO_3$	Ammonium carbonate
$(NH_4)_2SO_4$	Ammonium sulfate
NO_2	Nitrogen Dioxide
NO_x	Nitrogen Oxides
O	Oxygen
O_3	Ozone
OH	Hydroxyl
PAHs	Polycyclic Aromatic Hydrocarbons
PCC	Precipitated Calcium Carbonate
Pb	Lead
PM	Particulate Matters
RH	Relative Humidity
S	Sulfur
SO_2	Sulfur Dioxide
VOCs	Volatile Organic Compounds
W	Watt
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Clean and unpolluted air is basic requirement to support healthy human life. However, air pollution has become a challenge issue as it is driving by urbanization, economic development, transportation and motorization, energy consumption, and increase of urban population (Chen and Kan, 2008). It has been claimed that the greenhouse gases pollution will create intense heat waves frequently, and causes mortality problem especially among the poor and elderly (EPA, 2017). In Malaysia, the raising of the industrial section promptly due to the technology developed in recent years has led to environmental issues. When this manufacturing age came into view and science became more advanced, the environmental problems are associated, and one of the major concerns is air pollution generated by transport and industry sectors (Conserve Energy Future, 2017; Giz, 2006).

Air pollution can be defined as the degradation in air quality due the physical or chemical alterations resulted by natural processes or human activities (Mabahwi, Leh and Omar, 2015). Air pollutants such as nitrogen dioxide (NO_2), sulfur dioxide (SO_2), carbon monoxide (CO), carbon dioxide (CO_2), particulate matters (PM) and ozone (O_3) are regarded as the most common toxic gases in the ambient air (Chen and Kan, 2008). In 20th century, the realization of air pollution issue that should be limited was marked by a series of air pollution events (Stanek, et al., 2011). For example, one of the famous disease outbreaks happened in London (1952), where there was a severe air pollution causing 4,000 people to death prematurely in a week, followed by another 8,000 people in the month to come. In June 2013, Malaysia had also experienced the worst haze incident in 16 years, and the majority (60%) of the residents in Selangor area suffered from respiratory infections during that period. Moreover, the API value of Port Klang reached the very unhealthy level, which was 214 (Mabahwi, Leh and Omar, 2015). Besides, World Health Organisation (WHO) reported there were approximately 7 million people died annually due to the inhalation of air pollutants (Microbe Post, 2015).

Fossil fuel combustion for heating, electricity generation, transportation, and industrial sectors is the major source of air pollution. Based on World Energy Council (2013), it was stated that in year 2011, 82% of the total primary energy supply represented by fossil fuel burning (Perera, 2017). The database of latest urban air quality obtained from low- and middle-income countries also showed that 98% of cities with more than 100 thousands inhabitants do not meet the guidelines of World Health Organization (WHO) air quality, whereas in high-income countries, there is only 56%. The combustion of fossil fuels usually associated by the emissions of black carbon, polycyclic aromatic hydrocarbons (PAHs), particulate matters (PM), sulfur dioxide (SO_2), nitrogen dioxide (NO_2), mercury and carbon monoxide (CO), and lead (Pb) to multiple human health impacts (Perera, 2017).

The adverse health effects such as cardiovascular diseases, respiratory morbidity and mortality have brought the awareness in air pollution to the public (Mabahwi, Leh and Omar, 2015). Apart from that, air pollution also brings negative impacts to environment as well, where the toxic chemicals in the air will form acid rain, and cause destructions of crops, trees, farm, and animals. It can degrade the quality of water bodies, and causes harmful effects to human and animals that rely on these water bodies to survive (Choudhary, 2015). Some efforts can be done to control and reduce air pollution issues. In Malaysia, the emission of air pollutants from the industries must comply with the Environmental Quality (Clean Air) Regulations 1978 (DOE, 2010).

1.2 Source of Sulfur Dioxide

One of the concerned harmful gases that polluted the environment is sulfur dioxide. Sulfur dioxide can be released via natural and human activities. The major contributor of sulfur dioxide gas (SO_2) to the atmosphere is from burning of fossil fuels such as natural gas, coal, and oil. According to the Tropospheric Emission Monitoring Internet Service (TEMIS), there is 50% of the emission rate of SO_2 contributed from coal fired power stations annually, and the oil burning activities contribute another 25-30% (Newton, 2017).

Based on the SO_2 emission data in 2008, approximately 48% of the SO_2 emissions in Malaysia are generated by a total 41 power stations, which released about 78,416 metric tonnes of SO_2 to the atmosphere. Besides, the second major SO_2 contributor is the industrial processes such as services sectors and manufacturing sectors. **Figure 1.1** shows the sulfur dioxide emission in global from year 1990 to 2010. It can be clearly seen energy sector and industrial sector are the major contributors (Kimont, Smith and Cofala, 2013). Desulfurization by adsorption process is considered as a promising technique as it can achieve high efficiencies of gas removal, where the sulfur concentration can be reduced less than 1 ppm in ambient operating conditions (Aguiar and Coelho, 2017).

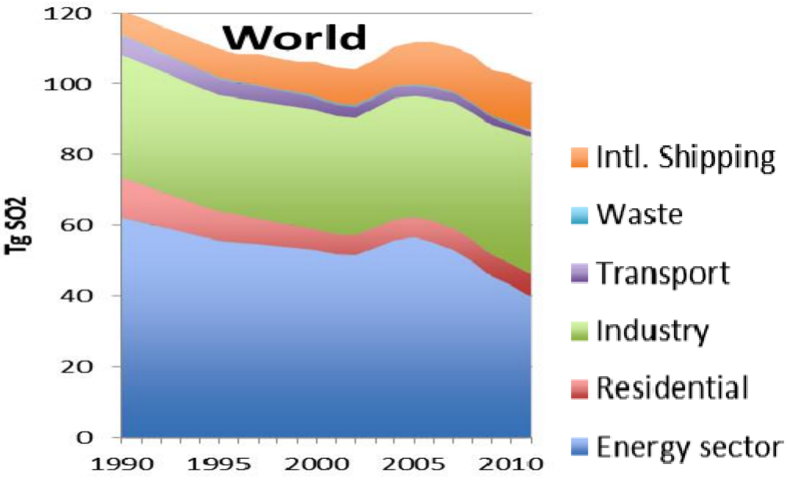


Figure 1.1: Sulfur Dioxide Emission by Sources from Year 1990 to 2010 (Kimont, Smith and Cofala, 2013)

1.3 Problem Statement

The problem of acid rain resulting by sulfur dioxide (SO_2) is one of the major concerned problems all over the world, especially in the countries of Canada, the eastern United States (US) and Scandinavia. In northeastern US, the acidity levels of rainwater had reached 10 to 100 times of normal rainwater. Due to the increased acidity of lake water, there is no fishes in more than 90 lakes found in Adirondack Mountains, New York State (Wang, Williford and Chen, 2004). In Malaysia, the emission of SO_2 in big cities such as Klang Valley was mainly due to high sulfur fuel dependency for industrial activities and electric power generation (Abdullah, Samah and Jun, 2012). It was also reported the overall air quality in Klang Valley (2009) was considered moderate, where only 5% of these days were considered unhealthy (Abdullah, Samah and Jun, 2012). Despite there is no online source provides exact data of the total emission of sulfur dioxide found in these few years, sulfur dioxide emission control still plays an important role especially in industrial sector. Exposure to SO_2 can cause respiratory problems and intension cardiovascular diseases (Roy and Sardar, 2015). Although the commercial calcium carbonate produced from natural limestone is abundant and has been using widely for sulfur dioxide removal, the price for one ton of calcium carbonate powder is high. Apart from that, limestone is not found anyway and it only happens in underlain areas by sedimentary rocks. Moreover, the limestone mining process can have adverse effects to the environment. It creates noise and dust pollutions from explosions during the mining process, and affects groundwater conditions (Seattlepi, 2018). To solve the costing and depletion of natural resource problems, calcium carbonate extracted from eggshell is proposed in this project to remove the SO_2 gas. Eggshell is considered as a waste product and is required to be disposed in landfill. In Malaysia, approximately 18,000 tons of solid wastes are generated daily, where 75% of the wastes are disposed at landfills without proper treatment (Jereme, et al., 2015). Therefore, reprocessing and reutilizing eggshell wastes is a good idea to reduce the amount of solid waste and meanwhile achieving sustainable development. A study that had been done on eggshell waste generation claimed that in India, the United States and the United Kingdom produce around 190000, 150000 and 11000 tonnes of eggshell waste per year respectively. Despite the eggshell waste can be utilised in different ways such as animal feeding, the majority is ended up in landfills (Yerramala, 2014). High amount of disposal costs are required to pay by the production industries every year (Glatz, Miao and Rodda, 2011). Due to the attached membrane on the eggshell, it tends to attach vermin and causes negative impacts on human health and environment (Yerramala, 2014). Hence, in this research, the major goal that needs to be achieved is to replace the commercial calcium carbonate with eggshells waste as an alternative.

1.4 Research Objective (s)

1. To test the potential of eggshell with and without membrane for SO_2 removal.
2. To investigate the effects of temperature, humidity and particle size for SO_2 removal.
3. To compare and characterize eggshell based $CaCO_3$ to commercial $CaCO_3$ (CCC).

1.5 Scope of Study

In this research study, eggshell waste was utilized as a raw material to remove sulfur dioxide by adsorption process. The removal efficiency of SO_2 calcium carbonate ($CaCO_3$) extracted from eggshells (with membrane, ESM and without membrane, ES) was observed and compared with commercial calcium carbonate (CCC). The effect of relative humidity (without RH and 40% RH), temperature (room temperature and 100°C) and particle sizes (<180 μm, <125 μm and <90 μm) was studied and evaluated. The determined optimal parameters was further tested with commercial precipitated calcium carbonate, and the removal efficiency was compared with the eggshell calcium carbonate. Characterization was done to justify the performance.

CHAPTER 2

LITERATURE REVIEW

2.1 Pollutants Released During Fossil Fuels Combustion

Fossil fuels has been used as the main sources for heat and electrical energy generations for long time. The fuels are included natural gas, coal, petroleum, bitumen, and shale oil consist materials such as metal, nitrogen and sulfur compounds besides the major constituents of carbon, hydrogen, and oxygen. During combustion, pollutants such as sulfur oxides, fly ash, nitrogen oxides (NO_x) and volatile organic compounds (VOCs) are released to the atmosphere, and cause environmental problems (Chmielewski, 2014). **Figure 2.1** below shows fossil fuel usage per capita in world's 20 largest population, US is the country that has the highest annual tonnes carbon emission per capita in 2014.

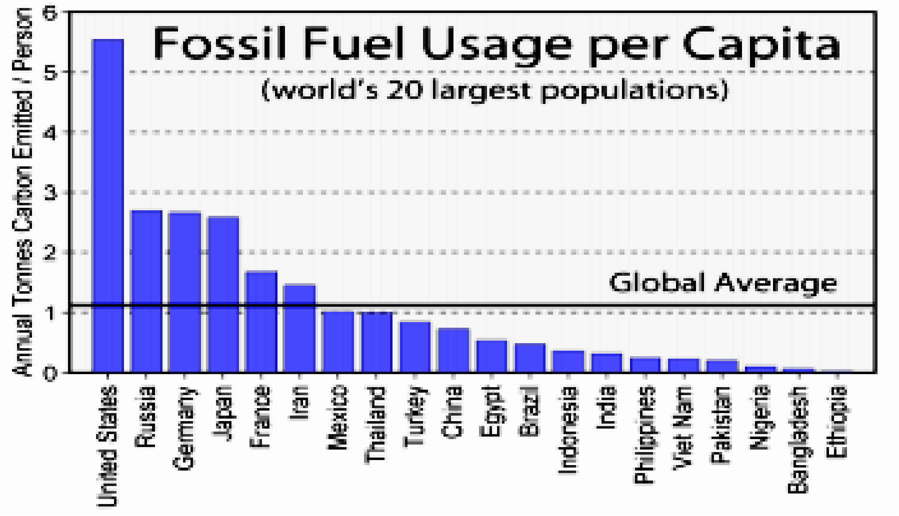


Figure 2.1: Fossil Fuel Usage per Capita in World's 20 Largest Populations (Rani, 2014)

National Ambient Air Quality Standards by US EPA have been recognised 7 common pollutants: carbon monoxide (CO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), particulates (PM), ozone (O_3), and lead (Pb). The general sources for each pollutants and the emission standards are shown in **Table 2.1** and **Table 2.2**.

Table 2.1: Common Air Pollutants and General Sources (EPA, 2015)

Air Pollutants	General Source
Carbon monoxide (CO)	Auto emissions
Nitrogen dioxide (NO_2)	Electric utilities, auto emissions
Sulfur Dioxide (SO_2)	Industries, electric utilities
Particulates	Various
Ozone	NO_x + VOC + sunlight
Lead	Lead smelters, leaded gasoline

Table 2.2: National Ambient Air Quality Standards (EPA, 2016)

Pollutants	Averaging time	Primary Standard Level
Particulate matter (10 μm in size)	Annual	75 μg/m^3
	24-h	260 μg/m^3
Sulfur oxides	Annual	80 μg/m^3 (0.03 ppm)
	24-h	265 μg/m^3 (0.14 ppm)
Carbon monoxide	8-h	10 μg/m^3 (9 ppm)
	1-h	40 μg/m^3 (35 ppm)
Nitrogen dioxide	Annual	100 μg/m^3 (0.05 ppm)
Ozone	1-h	240 μg/m^3 (0.12 ppm)
Hydrocarbons	3-h (6-9 A.M.)	160 μg/m^3
Lead	3 months	1.5 μg/m^3

The pollutants emitted to the atmosphere not only caused air pollution, but also contaminate water and soil. The emitted pollutants during combustion include carbon monoxide, sulfur oxides, carbon dioxides, nitrogen oxides, particulate matter, soot, and unburned hydrocarbon are known as primary pollutants. The further reaction of these pollutants will form secondary pollutants in the atmosphere, for example sulfur oxides and nitrogen oxides react with water will form acid rain. Moreover, it is estimated that about 50% of the gases emitted during fossil fuels combustion contributed to greenhouse effect (Rani, 2014). Therefore, the air pollutants emission control is important to minimize the occurrence of air pollution.

2.2 Sulfur Dioxide

Sulfur is one of the most abundant elements in earth's crust, where majority of this element happen in the form of sulfates, which commonly found in gypsum, $CaSO_4.2H_2O$. In the presence of 2000 ppm in water, calcium sulfate are soluble, and tends to contribute the hardness in groundwaters (Nevers, 2000). Sulfur dioxide is commonly applied on pulp and paper industry, food industry, and petroleum industry. Besides, sulfur dioxide also can be utilised in water, wastewater, and industrial wastewater treatment systems to reduce the residual chlorine (WBK & Associates Inc., 2003).

In last 150 years, the concentration of sulfur dioxide in the atmosphere has been increased rapidly due to industrial revolution. Before that, the major natural sources of sulfur dioxide were contributed by volcanic events, and the oxidation of reduced sulfur compounds resulted by oceanic phytoplankton (Andes and Kasgnoc, 1998; Bates et al., 1992). However, in order to satisfy the world needs, the natural deposits, pyrite and gases which consist sulfur element are extracted from earth's crust, and processed into raw materials that use for different purposes. During these processes, the sulfur compounds will be converted into sulfur dioxide (SO_2) and/ or hydrogen sulfide (H_2S) (Yavorskiy, Slyuzar and Kalymon, 2016).

Other than that, the anthropogenic activities such as biomass and fossil fuels burning, smelting of sulfidic ores in these modern days contribute about 70 to 80 Teragram of sulfur to the atmosphere annually, which is quadrupled the sulfur dioxide emissions from natural sources in the absence of volcanic events to the atmosphere every year (Macdonald, et al., 2004; Stern, 2005). One of the major concerns nowadays is the severe environmental problem that resulted from the generation of electricity by conventional power plants. For most of the developing countries, the environmental pollution issues are getting serious as these countries are highly relying on coal power generation which resulted the emission of sulfur dioxide due to the reason of abundant amount of natural coal (Salahudin, Abdullah and Newaz, 2013). It is estimated that in Asia, the emissions of sulfur dioxide had been increased from 17.1 million tons to 38.5 million tons in 1975 to

1995, with the increased rate of 4.1% annually (Cofala, et al., 2004). Moreover, in 2008, it was recorded that 48% of total sulfur dioxide emission in Malaysia released from power stations, and caused 78,416 metric tonnes of it emitted into the atmosphere. The second major contributor was related to industrial processes, which caused 23% (36,938 metric tonnes) of sulfur dioxide emission in the same year. The results were followed by the activities of motor vehicles and others, which showed 8% (12,865 metric tonnes) and 21% (33,694 metric tonnes) respectively (Salahudin, Abdullah and Newaz, 2013). In addition, based on the statistical data of Department of Statistics, Malaysia, SO_2 gas was found as the third highest gas emission from power plants and industrial activities in 2015, with a record of 209,156 tonnes (Department of Statistics, Malaysia, 2016). Generally, urban areas usually have been experienced the most serious air pollution problem caused by sulfur dioxide where fossil fuel is widely used for the purposes such as domestic heating purposes, or inadequate controlled combustion in industrial sectors (WHO Regional Office, 2000).

Sulfur dioxide tends to accumulate close to the ground level, whereby it is depending on several factors such as wind, humidity, temperature, and topography (The World Bank Group, 1999). When reacted with water, sulfur dioxide will form acid rain formed and bring adverse impacts to environment and human health. The acidic rainwater not only causing deforestation, but also altering the pH of waterways, leading to detriment of aquatic life. Despite sulfur is not the primary factor that causes plant injury compared to other pollutants such as ozone, it is believed that the input of sulfur to soil will result low yields in long term (The World Bank Group, 1999). Moreover, it will accelerate the corrosion of building materials and paints. In term of health, when human exposure to the sulfur dioxide gas, our respiratory system especially lung function will be affected. The symptoms of mucus secretion, coughing asthma, chronic bronchitis can be observed (Queensland Government, 2017). For human, the threshold of olfactory is 0.3 to 2.5 ppm sulfur dioxide. When its concentration reached 5 to 10 ppm, it will result irritation of respiratory tract, and more severe effects such as a severe, dry cough. Moreover, when SO2 concentration reached to 400 to 500 ppm, fatal may be resulted in short period of time if inhaled accidentally (Hasenberg, 2008).

2.2.1 Properties and Reactions of Sulfur Dioxide

Sulfur dioxide (SO_2) is a colourless gas, its smell and taste can be detected if its concentration is in the range of 1-3 mg/m^3. When the concentration has exceeded 10 mg/m^3, this gas will give a pungent and unpleasant odour (Armenta and Guardia, 2016). SO_2 gas is readily soluble in water, where its solubility enhances as there is decreasing of temperature but increasing of partial pressure. With its very stable chemically properties, it undergoes severe thermal dissociation when the temperature is above 2,273 K (Hasenberg, 2008; Ashar, 2016).

Sulfur dioxide in the atmosphere will transform into sulfur trioxide by photochemical or catalytic reaction. The resulted sulfur trioxide will be further hydrated by humidity into sulfur-dioxide aerosol. Besides, with the presence of alkaline particles in the air, sulfur dioxide will react with the particles to form sulfates, and the absence of these alkaline particles in the air will cause precipitation-water acidification, where acid rain is resulted in this process (Hlincik and Buryan, 2012). About 73% of sulfur dioxide emissions generated from combustion activities at power plants, and 20% of the emissions come from other industrial processes such as metal ore extracting (Roy and Sardar, 2015). During fuel combustion, about 95% of sulfur is oxidized to sulfur dioxide, and it will be further oxidized to sulfur trioxide with the presence of free OH and HO_2 radicals. Once the sulfur trioxide contacts and reacts with vapor in the clouds, it forms sulphuric acid or sulfites if reacted with dusts containing metal oxide (Krawczyk, et al., 2013). The reaction of water and sulfur dioxide raised great interests of industry sector due to its importance in the production of sulfuric acid. Another industrial interest is the reduction process of SO_2 with hydrogen, carbon or other carbon compounds. With the requirements of catalysts or high temperature or catalysts or both of them, the mixtures of elemental sulfur with hydrogen sulfide will be resulted. The end-products of carbonyl sulphide, carbon dioxide and carbon disulphide will be resulted as well if carbon or other carbon compounds was used as reducing agent for the reduction process (Hasenberg, 2008). **Table 2.3** below illustrated the properties of sulfur dioxide.

Table 2.3: Properties of Sulfur Dioxide (Ashar, 2016; Hasenberg, 2008)

Chemical Name	Sulfur Dioxide
Colour	Colourless
Odor	Strong choking smell
Taste	Acid taste
Molecular Formula	SO_2
Molecular Weight	64.058 g/mol
Boiling Point	-10 ^{o}C
Melting Point	-75.5^{o}C
Critical Density	0.525 g/cm^3
Critical Pressure	78.8 bar
Critical Temperature	157.5^{o}C
Standard enthalpy of formation	-70.94 kcal/mol
Specific heat, Cp (1013 mb)	At 0 ^{o}C : 586 K/ (kg.K) At 100 ^{o}C: 662 J/ (kg. K) At 300 ^{o}C: 754 J/ (kg. K) At 500 ^{o}C: 816 K/ (kg. K)

2.3 Sulfur Dioxide Removal Methods

Based on National Ambient Air Quality Standards, the primary standard levels of sulfur dioxide in atmosphere are 80 µg/m^3 annually and 265 µg/m^3 in 24-hour respectively (EPA, 2016). Besides, the recommended Malaysian Air Quality Guidelines stated that the standard levels of sulfur dioxide in ambient standard is 105 µg/m^3 in 24-hour (DOE, 2015). Due to the high emission rate of sulfur dioxide from industrial sectors, the implementation of rules and regulations is important to control the emissions. It had been over 150 years studied on the methods of SO_2 removal from furnace and boiler exhaust gases (Roy and Sardar, 2015). Some people reduce the concentration of sulfur dioxide at ground level by improving the conditions of emission, such as increasing the stack height, diluting sulfur dioxide with air, or increasing the speed of the flue gas. However, these measures are considered ineffective as they only favour in certain conditions (Kettner, 1965). For example, the method of emitting the flue gases via tall stacks is not suitable for the problems of long-distance transport and deposition of sulfur (The World Bank Group, 1999). Apart from that, this is not a control method as the magnitude of sulfur dioxide is only dispersed and diluted in the air (Pandey, et al., 2005).

Hitherto, there are several popular approaches for limiting the sulfur dioxide emission, which included the appropriate technology of combustion, the use of low sulfur content fuel, removal and reduction of sulfur in feed, and the emission control technologies (The World Bank Group, 1999). Presently, in most of the sulfur dioxide emissions control systems, sulfur dioxide reacts with calcium-based compound, and converts to calcium sulfite, $CaSO_3$. The major technologies of sulfur dioxide emission control are wet scrubbing, spray-dry scrubbing, oxidation and selective catalytic reduction. However, these removal methods have some disadvantages. Using wet scrubbing method to remove SO_2 gas tends to generate large amount of wastewater despite has high removal efficiency. Besides, spray-dry scrubbing has low removal efficiency, and can produce sludge during SO_2 removal process. Therefore, adsorption methods had become one of the most promising approach to remove SO_2 gas due to its low cost, low energy requirement, and ease of applicability in industrial areas (Zhou, et al., 2012). With high selectivity, high surface area and excellent regeneration capacity of the adsorbent characteristics, it can achieve high efficiencies of the adsorption process where the sulfur concentration can be reduced to less than 1 ppm (Melise and Gerson, 2017).

Desulfurization is a process to remove the sulfur compounds and elemental sulfur from solids, liquids and gases in power plants (Wang, Williford and Chen, 2005). FGD is an end-pipe-treatment where the flue gas is treated before emitted to atmosphere (Roy and Sardar, 2015). It has been widely installed in many industrial sectors for many years for sulfur dioxide removal (Dehghani and Bridganian, 2010). In industries, the SO_2 gas removal can be completed by the techniques such as gas-liquid reactions with liquid alkaline materials, or solid-gas reactions which involved inorganic sorbents. In some cases, it can be removed by conversion process, where catalysts are used to convert SO_2 into sulfuric acid (Karatepe, et al., 2008).

2.4 Adsorption

As mentioned earlier, many strategies had been suggested to control the emissions of SO_2, which includes scrubbing method and use low sulfur content fuels. Among all those strategies, the most economical and popular method is the addition of selective adsorbents (Song, etc., 2014). Adsorption-based gas separation is one of the important techniques in industry. The process of adsorption can be defined as a surface phenomenon where a multi-component fluid mixture is attached or attracted to a solid adsorbent surface (Foo and Hameed, 2010). Adsorptive separation plays a vital role in environmental technologies, as it has been applied in different sectors such as CO_2 capture, H_2 and CH_4 purification, desulfurization of fuels, removal of CO for fuel cell technology, etc (Li, Kuppler and Zhou, 2009). Some adsorbents are applied on storage or separation processes of gas, liquids purification, drug delivery controlling, and pollution control. To date, the adsorption of gas has become one of the popular procedures for governing the surface area and pore size distribution of different types of powders and materials (Rouquerol, et al., 2014). Carbon based, silica based and metal organic frameworks (MOFs) are the most common adsorbents that used to remove acid gases. Despite some solvents such as diethylamine (DEA) and monoethanolamine (MEA) has high selectivity on the separation of acid gases in adsorption process, it requires high demand of energy and space, which cause the solvents high costs (Bamdad, Hawboldt and MacQuarrie, 2018).

The adsorption process can be classified into physisorption and chemisorption. The concerned features that are interested in adsorption process are included interface characteristics, thermodynamics, adsorption isotherm, and interactions of adsorbate-adsorbent (Guru and Dash, 2014). Apart from excellent adsorption capacity and selectivity, the adsorbent for gas adsorptive separative must also possess good adsorption kinetics and regenerability. Therefore, high surface area and large pore size of adsorbent are favourable in order to provide good adsorption capacity (Li, Kuppler and Zhou, 2009). The mechanisms of gas adsorptive separation by a porous material involved four effects. Firstly is the sieving effect of molecular. Some components of gas mixture are prohibited diffusing into the pores of adsorbents, and only allowed to adsorb certain other components. Second, based on thermodynamic equilibrium effect, only certain components are preferable to attach on the surface of adsorbent, due to various adsorbate-surface and/or adsorbate packing interactions. Third, the kinetic effect caused by different diffusing rates of components only allow certain of them entering the pores and adsorbed faster than others. Forth, is the quantum sieving effect, where the light molecules are allowed to be separated, due to different diffusing rates in narrow micropores (Yang, 2003; Keller and Staudt, 2005). The shape and cross-sectional size (collision diameter) of adsorbate molecule are the key factors of selective adsorption, where the molecular sieving may be affected by temperature if the pore is sensitive to it (Li, Kuppler and Zhou, 2009).

In other way, the equilibrium adsorptive separation allows all the component of gas mixture to pass as the adsorbent has large pore for the components, and the separation quality is greatly depends on the interaction between the adsorbate and adsorbents surface. Besides equilibrium separation, kinetic separation is another option as well. Nevertheless, the pore size of adsorbent is a key factor and needs to be governed precisely between kinetic diameters of two molecules that require to be separated (Yang, 2003).

2.4.1 Chemisorption and Physisorption

As mentioned earlier, adsorption process can be classified into two types: chemisorption and physisorption. Chemisorption described the adsorption process where chemical bonds are formed between the surface of adsorbent and adsorbate. Generally, it can be considered as chemical reactions where the energy of chemisorption may be endothermic or exothermic. The fundamental step of this adsorption process usually involved high activation energy, hence it takes longer time to achieve the true equilibrium. Chemisorption often requires high temperature as the increasing of temperature will often increase the adsorption process. Thus, the temperature is said to be a key factor to influence the efficiency of adsorption. Besides, the chemisorption is allowed to occur only under high vacuum or temperature in extreme conditions, or by some appropriate chemical treatment of the surface. (Somasundaran, et al., 2009) The increase of surface area of adsorbents will increase the chemisorption process, as the valence bonds connect the adsorbed molecules to the surface of adsorbents.

Physisorption involves the Van der Waals forces (intermolecular forces), which do not alter the electronic orbital patterns of the species. The adsorbate and adsorbent require the energy of interaction with same magnitude order, however is larger than the condensation energy of the adsorptive. Unlike chemisorption process, physisorption does not require activated energy, and only involve low temperature. Hence, the physisorption process is increased with the decrease of temperature (Al-Anber, 2011). The weak forces performance of attraction between molecules causes the physisorption is nonspecific. In addition, the adsorbed molecules are allowed to move freely about over the solid surface and can return to its nature as the small enthalpy change is insufficient to break the molecular bond (Al-Anber, 2011; Atkins and Paula, 2009). Apart from that, according to IUPAC recommendation (1985), the pores size of the solid surface can be classified as shown in **Table 2.4** below:

Table 2.4: IUPAC Recommendation (1985) on Pore Size Classification (Thommes, et al., 2015)

Pores with widths	Class
More than 50 nm	Macropores
In the range of 2 to 50 nm	Mesopores
Not more than 2nm	Micropores

2.4.2 Factors Affecting Adsorption

The adsorption process is determined by several key factors, including surface area of adsorbent, adsorbent particle size, contact time, molecular size with respect of pores size, degree of ionisation of adsorbate, pH, initial concentration, and dosage.

First, the larger surface area is favored as it provides greater adsorption capacity. In contrast, the reducing of particle sizes will reduce the internal diffusion and mass transfer limitation of adsorbate to adsorbent. Li, Kobayashi and Hu (2008) had concluded that the BET surface areas had rose 8.3 times with the particle size of coal increased from the diameter of 1 mm to 105 um. Meanwhile, the cumulative pore volume of the coal particles also increased 8.8 times.

Second, the higher adsorption efficiency can be achieved by smaller particle sizes, and gives higher adsorption rate as it provides short path to travel inside the small particle size structure. A research found that the removal efficiency of Fe^{3+} ions achieved its maximum with the particle size 45 μm rather than 125 and 250 μm as most of the internal surface of smaller particles is used for adsorption. Besides, Al-Harahsheh, et al. (2014) investigated that the decrease in particle size of zeolite tuff resulted longer breakthrough time during SO_2 adsorption process. Third, the completion of adsorption process is determined by the contact time. The longer contact time will have more complete adsorption process (Al-Anber, 2010).

Forth, in the aspect of molecular size with respect to pore size, large molecules may reduce the adsorption efficiency if the pores size is too small. Thus, the appropriate pores size should be selected. Besides, compared with neutral molecules, more highly ionized molecules are more likely to be adsorbed to a smaller degree molecules. Nevertheless, the degree of ionization is influenced by the pH, and therefore affects the adsorption process (Al-Anber, 2011). In the industrial practice, the pH required for the slurry for desulfurization process should maintain at 6.0 to 6.5 to ensure the efficiency and also to enhance the utilization of the adsorbent and reduce the running cost (Shen, et al., 2013).

Moreover, the initial concentration tends to affect the competitive diffusion process through the pores as the available sites of adsorption is reduced. Therefore, in high concentration, the adsorption efficiency will be reduced compared to in low concentration. For example, Shen, et al. (2013) proved that the high initial concentration of SO_2 will often lead to the increment of the total load despite can enhance the SO_2 driving force. Thus, the efficiency of desulfurization will be reduced with increasing of initial concentration of SO_2. Apart from that, the dosage plays a vital role in adsorption process as well, because of the increment of mass available will offer more contact surface to the adsorption (Al-Anber, 2011).

According to Li, Kobayashi and Hu (2008), steam activation is one of the vital factors affecting the flue gas adsorption process. When there is high temperature in the reactor, different surface tension will be resulted between steam (H_2O) that entering into the reactor and the coal (adsorbent). The surface pore width of coal can be widened as a result of vapor function due to the chemical reaction of carbon.

2.5 Adsorption Isotherm

Adsorption isotherm can be described with the relation between the amount adsorbed and the equilibrium gas pressure at constant temperature (Thommes, 2015). The process can be represented by the Equation (**2.1)** as shown below:

$$A\ (gas) + M\ (surface) \leftrightarrow AM\ (surface) \tag{2.1}$$

In equilibrium of dynamic, the fractional coverage of the surface, θrelies upon the overlying gas pressure. And the variation of the fractional coverage at particular temperature is known as adsorption isotherm (Atkins and Paula, 2009).

The originally developed adsorption isotherm to describe the gas-solid-phase adsorption is Langmuir isotherm which originally presented by Irving Langmuir (1916). This approach was assuming the system is in dynamic equilibrium (Yang, 2013). The Langmuir theory introduced the adsorption mechanisms included where it is only one type of adsorbing site, or more than one type of adsorbing site, more than one molecule can be accommodated in each site, dissociative adsorption, multilayer adsorption occurs, and the surface of adsorption is amorphous but is continuum. Besides, the Langmuir isotherm can be applied to evaluate the maximum adsorption capacity interrelated to complete monolayer coverage on calcium carbonate surface. The Langmuir equation **(2.2)** can be expressed as:

$$R_L = \frac{1}{1+KLCo} \tag{2.2}$$

Where K_L represents the Langmuir constant (L/mg), C_O as the adsorbate initial concentration (mg/L) and R_L refers to separation factor. The value of R_L always indicates the favourable level of adsorption, which is further explained in **Table 2.5**:

Table 2.5: Classification of Separation Factor (R_L)

Value of Separation Factor (R_L)	Description
$R_L > 1$	Unfavourable adsorption
$R_L = 1$	Linear adsorption
$0 < R_L < 1$	Favourable adsorption
$R_L = 0$	Irreversible adsorption

2.6 Adsorbents for SO_2 Control

Several adsorption process on sulfur dioxide had been published in past few years. **Table 2.6** shows different types of adsorbent used for sulfur dioxide removal.

Table 2.6: Types of Adsorbent Used for Sulfur Dioxide Removal

Adsorbents /Chemicals	Removal efficiency	References
Palm Shell Activated Carbon for SO_2 and CO removal	75% of CO and 100% of SO_2.	Akbar, et al., 2013
Graphene oxide (GO) and HNO_3 modified carbon black (mCB)	96.1% to 98.4%	Zhang and Wang, 2016
Waste oyster shell as SO_2/NO_x removal sorbent	0.78 mmole/g	Jung, et al., 2012
SO_2 adsorption using hydrogen peroxide solution	95%	Dina, et al., 2016
Activated coke for SO_2 adsorption	100 mg-SO_2/ g-Activated coke	Li, Kobayashi and Hu, 2007
SO_2 absorption and desorption using hydroxyl ammonium ionic liquid	The ionic liquid can be recycled four times to achieve more than 90% SO_2 recovery rate	Yuan, Zhang and Lu, 2007
Low cost adsorbents (waste materials such as orange peel powder, mango bark dust, horse gram seed powder, mixed algae, neem bark dust, ragi seed powder, neem leaf powder, pineapple peel powder, and custard apple leaf powder) for SO_2 controlling	Sulfur dioxide removal efficiency ranged from 74% to 98%.	Gandhi, Priyanka and Sirisha, 2012
Biochar from biomass waste	9.75 mg/g of SO_2 adsorption capacity	Iberahim, Sethupathi and Bashir, 2016.
Activated carbons	Range from 184.9 to 355.1 mg SO_2/g	Karatepe, et al., 2008.
Fly ash and $CaCO_3$ compound	Desulfurization rate reached 94%	Zhai, et al., 2017

Dina, et al. had conducted a research using hydrogen peroxide to remove SO_2. Despite it performed well in adsorbing sulfur dioxide gas, however, it is considered a costly method compared to using calcium carbonate. Li, Kobayashi and Hu (2007) prepared activated coke for SO_2 adsorption. The well-developed micropore structure with larger specific surface area of activated cokes performed well in the sulfur dioxide adsorption. Nevertheless, the intensification of activation process always resulted unsatisfied mechanical strength and decrement of granule size. In addition, higher amount of carbon losses during activation process and often resulted product with higher content of ash (Jastrzab, 2012). Yuan, Zhang and Lu (2007) proposed the concept of using hydroxyl ammonium ionic liquids for sulfur dioxide absorption and desorption. Despite hydroxyl ammonium ionic liquids can be recycled four times and gave excellent results in sulfur dioxide recovery, the formation of hydroxyl ammonium ionic liquids is tedious and pricey as it was prepared under neutralisation process with ethanolamine in ethanol with different acids. In addition, biochar with heating temperature at 405 ^{o}C, heating rate 20 $^{o}C/min$ and holding time of 88 min was resulted 9.75mg/g of SO_2 adsorption capacity (Iberahim, Sethupati and Bashir, 2016). It was also determined with the optimum ratio 1: 1 of fly ash and $CaCO_3$ compound and the mole ratio of Ca/S equal to 1.024, the desulfurization rate could achieve up to 94% (Zhai, et al., 2017).

There are some literature sources that had been mentioned on the disadvantages of using calcium carbonate for sulfur dioxide adsorption, however it has been widely used for decades due to highly available, low cost, well-developed technology of calcium-based adsorption and simple preparation of materials.

2.7 Calcium Carbonate

Calcium carbonate, $CaCO_3$, is one of the natural sources that comprises more than 4 percent of the earth crust. Its natural forms are generally found in marble, limestone, chalk, and resulted from the sedimentations of coral and shells over millions of years

(Mathur, Jakhar and Mathur, 2016). Calcium carbonate is an important biological system component, as it can be found in pearls, shells of marine organisms, and eggshells (Beruto and Giordan, 1993). Calcium carbonate from limestone is extracted by quarrying, conventional blasting, crushing and screening techniques (Poullikkas, 2015). The natural forms of calcium carbonates have the most common crystal arrangement structure, which is in hexagonal form of calcite. However, there are some with less common structure, which are in aragonite form with a clustered or discrete needle, orthorhombic crystal structure. The physical properties of calcium carbonate is white in colour, non-toxic and odourless. This natural's abundant raw material is composed three important elements for organic and inorganic matter in this planet, which are calcium, carbon and oxygen (BCCF, 2017).

Calcium carbonate is basically soluble with effervescence in acids such as hydrochloric, but is insoluble in ethanol and water (EFSA, 2011). Calcium carbonate can be obtained and manufactured from natural limestone by undergone the following industrial processes included: calcination process to produce quicklime (CaO) and CO_2, hydration process to transform CaO into slaked lime slurry ($Ca(OH)_2$), and carbonation reaction process to produce calcium carbonate ($CaCO_3$) by bubbling CO_2 through an aqueous slaked lime slurry (Domingo, et al., 2004). These processes can be represented by chemical equations below (Mathur, Jakhar and Mathur, 2016):

Calcination process in kiln: $CaCO_3 \rightarrow CaO + CO_2$ (2.3)
Slaked lime formation: $CaO + H_2O \rightarrow Ca(OH)_2$ (2.4)
Carbonation reaction: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3$ (2.5)

2.7.1 Application of Calcium Carbonate

It is a long history for people using calcium carbonate. Since 40,000 BC, calcium carbonate had been utilised for prehistoric cave painting purposes and to this present day, it is applied to modern paper and plastic manufacturing (BCCF, 2017b). In market, there are three types of commercial calcium carbonate: calcium carbonate powder, precipitated calcium carbonate (PCC), and dolomite. Calcium carbonate, or after calcination to lime, has been widely applied in the fields of chemical engineering, environmental engineering, and bioengineering due to its appealing applications. The usage of calcium carbonate is tabulated in **Table 2.7** below. It had been reported that calcium carbonate performs valuable applications in water purification field (Declet, Reyes and Suarez, 2016).

Table 2.7: Usage of Calcium Carbonate in Different Sectors (Kundig, Buhler and Surbeck, 2013)

Specification	Purpose
Iron and steel industry	● Metallurgical process
Chemical industry	● Wastewater purification
Construction mineral industry	● Production of calcareous sandstone and lime-bound aerated concrete as building materials ● Act as aggregates for artificial stones
Agricultural	● Animal feed ● Prevent acidification of soil.

As mentioned in **Table 2.8**, natural calcium carbonate is widely used for different sectors. Apart from what had been mentioned above, calcium carbonate is also a major adsorbent used in industrial sectors to remove sulfur dioxide. Nowadays, in most of the sulfur dioxide control systems, calcium-based compounds will be added to the system and reacts with sulfur dioxide to convert to calcium sulfite, $CaSO_3$. The major technologies of sulfur dioxide emission control are listed in **Table 2.8** below:

Table 2.8: Major Technologies of Sulfur Dioxide Emission Control in Industrial Sectors

Technology	Sorbent type	Adsorption capacity	Reference
Wet-flue gas desulfurization	Limestone or lime slurry	60-97%; The efficiency can be maximized up to 99% by enhancing with magnesium	Zivkovic, 2014
Dry-flue gas desulfurization	Lime or limestone or dolomite or sodium-based component	50-60%	Poullikkas, 2015; Roy and Sardar, 2015
Spray dry scrubbers (semi-dry process)	Calcium oxide or lime	90-95%	Poullikkas, 2015
Sorbent injection process	Hydrated lime or limestone	50%; 30-70%	Poullikkas, 2015; Roy and Sardar, 2015

The problem of natural calcium carbonate depletion started to raise a concern. Besides, harvesting the natural limestone will destroy the aesthetic of the nature as well. The quarrying process of limestone is commonly associated with climate and environmental burdens, which include the contamination of soil, water, air (Kittipongvises, 2017). Therefore, it is important to seek for its substitute which is not only economical but sustainable. In this research, calcium carbonate extracted from eggshell waste is proposed as the substitute of commercial calcium carbonate.

2.8 Eggshell Waste Production

It has been some time people start to turn waste products into useful materials. The interest of finding new materials that are sustainable has constrained the industries to transform their approach to recyclability and reusability (Cree and Rutter, 2015). Abundant volume of eggshell waste has being produced every day from world's egg production industries (Linden, 2009). Compared with year 1990, the consumption of eggs in 2009 had risen to 8.9 kg per capita per year, which is around 41% of increment since 1990 (Quina, Soares and Quinta-Ferreira, 2016). Every year, it costs approximately $100,000 has spent by companies to dispose the eggshell wastes in landfill. In Malaysia, there is about 642, 600 tonnes of annual egg production, and about 70, 686 tonnes of eggshell waste production (Rohim, 2014). Moreover, the eggshell waste is rejected by the owners of landfills as it attracts rats and other pests due to its protein in the membrane (Sonenklar, 1999). This disposal method becomes a problem as it affects public health, contaminates water resources, and pollutes our environment as well (Meski, Ziani and Khireddine, 2010). There are several traditional methods to dispose the eggshell waste other than landfill, such as composting, rendering, and incineration (Das, et al., 2002). Hence, eggshells has been suggested to be recycled to improve the waste management (Abdulrahman,, et al., 2014). Moreover, eggshell wastes had been proved as a low-risk material which falls in Category 3 in animal by-products (ABP) by the European Union (EU) (Quina, Soares and Quinta-Ferreira, 2016).

2.8.1 Calcium Carbonate in Eggshell

Based on literature, chicken eggshell composed of ceramic materials composed by 3 layered structure, which are cuticle (outer surface), a spongy layer and inner lamellar layer (Tsai, et al., 2006). A matrix constituted of protein fibers conjoined to calcite ($CaCO_3$) crystal is formed on the spongy and lamellar layers, with there are numerous circular pores present to allow gaseous exchange throughout the eggshell (Tsai, et al., 2006). It is reported that the protein fibres represent approximately 11% of the total weight of eggshell (Meski, et al., 2011; Oliveira, et al., 2013)A good quality eggshell produced from commercial egg industry has roughly 2.2g weight of calcium in the form of $CaCO_3$. For every 5.5 grams, the dried eggshell contains about 94-95 % of calcium carbonate (Butcher and Miles, n.d.). The other components of eggshell are organic substances such as type

X-collagen, sulfated polysaccharides, and other protein (~4%), calcium phosphate (~0.76%), and magnesium carbonate (~1.4%) (Schaafsma, et al, 2000; Hassan, et al., 2013). However, the quality of the eggshells is dependent and affected by several factors such as management practice of industries, environmental conditions, adequacy of nutrition, breeding, and flock health problem (Butcher and Miles, 1990). Comparing with calcium carbonate that extracted from oyster shells, eggshell has an advantage as it does not contain toxic elements such as cadmium, mercury, and aluminium that found in oyster shells (Murakami, et al., 2007). As eggshell does not contain impurities such as sands, clays and other minerals that present in quarried limestone, it enables to produce a purified form of mineral calcite (Cree and Rutter, 2015) The traditionally useless eggshell wastes are generally disposed in landfills, causing environmental odor problem as they are dumped without any pretreatment (Gao and Xu, 2012).

It had been reviewed that calcium carbonate in eggshell can be converted to calcium oxide through calcination process with temperature over 800 ∘C. Meantime, high usage demand of calcium oxide that produced from limestone will cause environmental problem. As limestone is non-renewable resource, high demand of natural limestone for different purposes will eventually cause rapid depletion (Rohim, et al., 2014). A rough estimation was reported that the production of worldwide mining of $CaCO_3$ is around 15 billion tonnes annually (The Essential Chemical Industry, 2016). Eggshell consists calcium carbonate as its main components, whereby its chemical composition is similar to limestone. Thus, it is believed that eggshell can be substituted to natural limestone. Despite it is found that the density of $CaCO_3$ (0.4236 g cm^{-3}) extracted from eggshell is relatively low than the density of mineral $CaCO_3$ (0.467 g cm^{-3}) (Hassen, et al., 2015), it is expected to have the same effect as commercial calcium carbonate in removing sulfur dioxide. The other usage of eggshell is shown in **Table 2.9**.

Table 2.9: Usage of Eggshell

Eggshell raw materials	References
Food additive production for human	Oliveira,et al, 2013
Food additive production for animal	Ruff, et al., 2012
Soil amendment	Yoo, et al., 2009; Tsai et al., 2008a, 2008b; Elwakeel and Yousif, 2010; Cordeiro and Hincke, 2011.
Ingredients of cosmetics	Cordeiro and Hincke, 2011
Catalysts	Laca, Laca and Diaz, 2017
Sorbents for heavy metal (Cr (III))	Chojnacka, 2005
Replacement in Portland cement mortar	Pliya and Cree, 2015
Eggshell powder as adsorbent for Fluoride removal	Bhaumink, et al., 2012
Lime/limestone scrubbing	Roy and Sardar, 2015

2.8.2 Eggshell Used as Adsorbent

It is reported that the low-cost adsorbents should require simple processing, abundant in nature, or is a waste or by-product from industrial sectors (Chojnacka, 2005). Presently, some literature had been reported on using eggshell as adsorbent in different fields, which is summarized in **Table 2.10**. Witoon (2011) reported that calcined eggshell can be used as calcium-based sorbent (CaO) to capture carbon dioxide from combustion gases. Compared to other conventional technologies, using eggshell waste as sorbent can reduce the cost during the process of gas capture. Witoon had found that the capture capacity of calcined eggshell sorbent performed better than commercial calcium carbonate due to larger exposed surface for CO_2 reaction. Flores-Cano, et al. (2013) studied the removal of cadmium (II) from water pollution sources using eggshell. Eggshell was sieved into 0.95 mm average particle diameter and dried at 100 ^{o}C for 24 hours. The results obtained for nonreversible mechanism is 68% and reversible mechanism is 32%. Based on the research done by Kose and Kinanc (2011), calcined eggshell was used as adsorbent for phosphate removal in water bodies' source. The adsorption capacity of calcined eggshell is up to 99% in the pH 2 to 10. Giraldo and Moreno-Pirajan (2013), the activated carbons obtained from eggshell have well-developed pore structure and high adsorption capacities, and its sorption capacity of phenol uptake is 192 mg/g. Pramanpol and Nitayapat (2006) studied the use of eggshell as adsorbents for reactive dye (C.I Reactive Yellow 205) removal. More than 72 to 99% of the Reactive Yellow 205 dye was adsorbed at equilibrium within initial range of concentration from 20 to 100 mg/L. Carvalho, et al. (2011) evaluated the adsorption capacity of the calcined eggshell powder was in removing copper and aluminium. The result showed that eggshell performed great in removing several pollutants from various types of aqueous system. Flore-Cano, et al. (2013) examined the chicken eggshell sorption mechanism of cadmium (II) from aqueous solution. It was discovered that the adsorption mechanisms of cadmium (II) is relied to precipitation and ion exchange. The contribution of reversible mechanism was 32% and the contribution of non-reversible mechanism was 68%. It was also reported that $(Cd/Ca)CO_3$ was precipitated on the eggshell surface during the adsorption process. Arunlertaree, et al. (2007) studied the removal of lead using chicken and duck eggshells by investigating the effect of parameters such as contact time, initial pH, types of eggshell and dosage. The study found 1.0g/ 100 ml was the optimum dosage of wastewater with 90 minutes of contact time, with the removal efficiency of 78.03%. The study of Habeeb, Yasin and Danhassan (2014) had proven that the calcined chicken eggshell has adsorption capacity of 2.1 mg/g to remove H_2S in wastewater. Their research indicated eggshell can be used as an economic adsorbents for the removal of H_2S.

Table 2.10: Eggshell as Adsorbent to Treat Different Compounds

Type	Specification	Sorbent	Treatment	Field	Removal Efficiency	References
Gas	Carbon dioxide	Eggshell, CaO	Calcination at 900 ^{o}C	Fossil fuel combustion	Removal efficiency is not clearly stated; ES sorbent has 1.6 times of sorbent stability after 11 carbonation cycles.	Witoon, 2011
Heavy metal	Cadmium (II)	Eggshell $CaCO_3$	Raw chicken eggshell dried at 100 ^{o}C	Wastewater	3.82 mg/g (pH 6, 35^{o}C)	Flores-Cano, et al., 2013
Anion	Phosphate	Eggshell, CaO	Calcination at 800 ^{o}C	Wastewater	23 mg/g under 25 ^{o}C	Kose and Kivanc, 2011
Organic pollutant	Phenol	Eggshell, activated carbon	Activated under 973K	Wastewater, water source	119.98mg/g	Giraldo and Moreno-Pirajan, 2013
Organic dye	C.I. Reactive Yellow 205	Eggshell, eggshell membrane	Raw eggshells fried at 105 ^{o}C	Industrial wastewater	72-99%	Pramanpol and Nitayapat, 2006
Heavy metal	Lead	Eggshell	Air dried and incubated at 40 ^{o}C	Battery manufacturing wastewater	78.03%	Arunlertaree, et al., 2007
Hazardous Gas	Hydrogen sulfide	Eggshell	Raw eggshell, activated eggshell and calcined eggshell	Wastewater	2.1 mg/g (calcinate)	Habeeb, Yasin and Danhassan, 2014

2.9 The By-Product: Gypsum

Some people always criticized using calcium carbonate to remove sulfur dioxide as it produces gypsum, which also known as calcium sulfate dihydrate ($CaSO_4. 2H_2O$) as the by-product. However, due to the low cost application and easy to access the material, it had been widely used in wet and dry FGD.–It is expected in future 10 years, the FGD gypsum production will be doubled due to the needs of scrubber to the rapid increase of coal-fired power plant. Although there is a strong demand for FGD gypsum in the aspects of plaster, plasterboard, and cement manufacture usages, the current uses of FGD gypsum is believed will not be able to consume all the new created gypsum in future (Dunster, 2007). Only part of the total amount of FGD gypsum was put to valuable use, the remainder was always landfilled (Environmental Protection Agency, 2008). Fortunately, it is found that FGD gypsum has the similar function as mined gypsum in enhancing the production of crop. Therefore, it can be used as a replacement of commercial mined gypsum to prevent both water and energy intensive mining activities related with the gypsum extraction (Chen and Dick, 2011). According to Li, et al. (2015) research, the FGD gypsum and fly ash produced from pulverized -coal combustion power plant can be utilized for manufacturing fire-resistant panels, as insulation construction materials with high economic value and low environmental implication. One of the famous application of the waste gypsum is converted to the fertilizer ammonium sulfate $(NH_4)_2SO_4$) (Song, et al., 2013). The chemical equation of the fertilizer formation is as below:

$$CaSO_4. 2H_2O + (NH_4)_2CO_{3\,(aq)} \rightarrow CaCO_{3\,(s)} + (NH_4)_2SO_4 + 2H_2O$$

Up to 99% purity of ammonium sulfate can be produced in this reaction. Apart from high purity, the reaction produces ammonium sulfate of high yield, and the reaction rate will be increased with the temperature (Burnett, Schultz and Hull, 1996). Other usage of FGD gypsum has been reported as tabulated in **Table 2.11.**

Table 2.11: Usage of FGD Gypsum for Different Purposes

Materials	Purpose	References
FGD gypsum and fly ash	Fire-resistance panels manufacture	Li, et al., 2015
FGD gypsum	Remove Pb(II) and Cd(II) from wastewater	Yan, et al., 2015
FGD gypsum	Conserve water and reduce agricultural soil erosion in Georgia	Truman, et al., 2010
FGD gypsum	Used as an admixture in cement and concrete	Guo and Shi, 2007
FGD gypsum	Used as reactive ingredient in a ditch filter to remove phosphorus	Bryant, et al., 2012

CHAPTER 3

RESEARCH METHODOLOGY

In this chapter, the experimental procedures and experimental setup were shown. There was 7 different sections discussed in detailed which including materials, apparatus, preparation of eggshell based calcium carbonate powder, experiment procedure, eggshell based calcium carbonate powder characterizations and adsorption capacity. **Figure 3.1** is a flow chart showed a brief procedure of this research project.

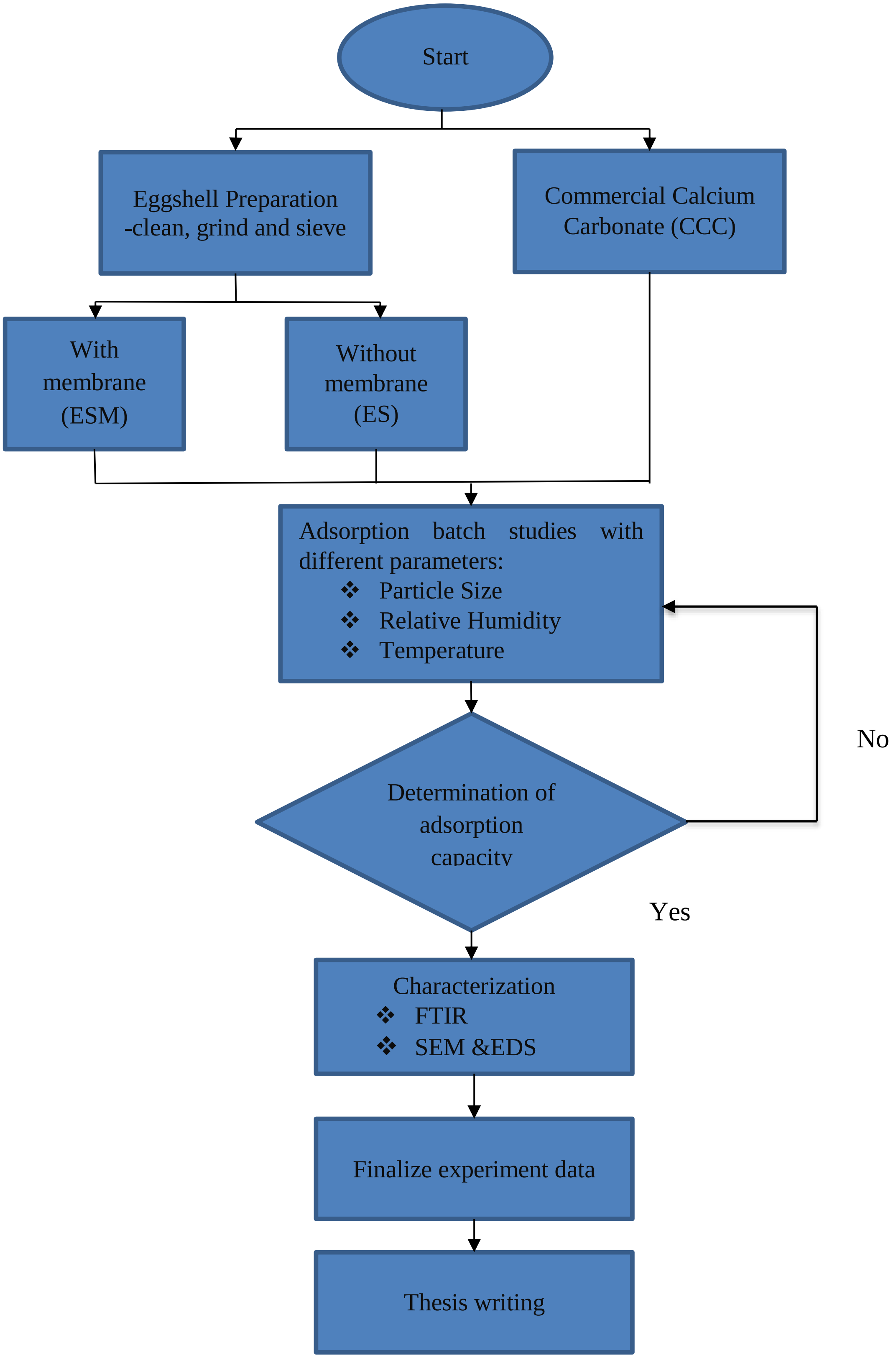


Figure 3.1: **Flow Chart of Experiment Procedure**

3.1 Materials

The materials involved in this research study is listed in **Table 3.1**.

Table 3.1: List of Materials for Research Study

Materials	Manufacturer/ Supplier	Purity (%)	Remark
Sulfur Dioxide Gas	LINDE MALAYSIA Sdn. Bhd.	99	Compressed gas of 2000 ppm
Nitrogen Gas	LINDE MALAYSIA Sdn. Bhd.	99	-
Eggshell (ground)	Restaurants and burger stalls	~94	Brown colour eggshell
Commercial Calcium Carbonate	Irama Canggih Sdn. Bhd.	99	Light Precipitated

3.2 Apparatus

In this research study, the apparatus used were listed in **Table 3.2**.

Table 3.2: List of Apparatus

Apparatus	Purpose	Manufacturer
1. **Grinder**	Eggshell grinding	Retsch ZM 200
2. **Mortar**	Further grinding to obtain desired particle sizes	-
3. **Sieve Vibrating Machine**	Sieving eggshell powder into different sizes	Fisher Scientific (M) Sdn. Bhd.
4. **Oven**	Drying samples	Kensains Sdn. Bhd.
5. **Gas Analyzer**	Adsorption capacity testing	VARIO plus SE
6. **Thermostatic Bath**	Control relative humidity	Tech-Lab MFG Sdn. Bhd.

3.3 Preparation of Eggshell Based Calcium Carbonate Powder

The eggshell wastes were collected from few places such as restaurants and burger stalls. The attached impurities on the eggshells were cleaned with clean tap water before crushing to prevent decomposition (Elkady, Ibrahim and El-Latif, 2011). In this study, two type of eggshell samples were prepared: eggshells with membrane attached (ESM) and eggshells without membrane attached (ES). The latter sample's membrane was removed by hand before crushed into small pieces. After that, the crushed eggshell samples were grinded into powder form using grinder. The eggshell powder was eventually prepared for sieving into different fractions <180 μm, <125 μm and <90 μm mesh size particles using sieve analysis vibrating machine. The samples were dried at 105 ^{o}C for at least 24 hours to remove the moisture content completely. It was presumed that the calcium carbonate constituent in the prepared eggshell powder was about 94% as studied in literature review. The preparation steps are illustrated in **Figure 3.2**.

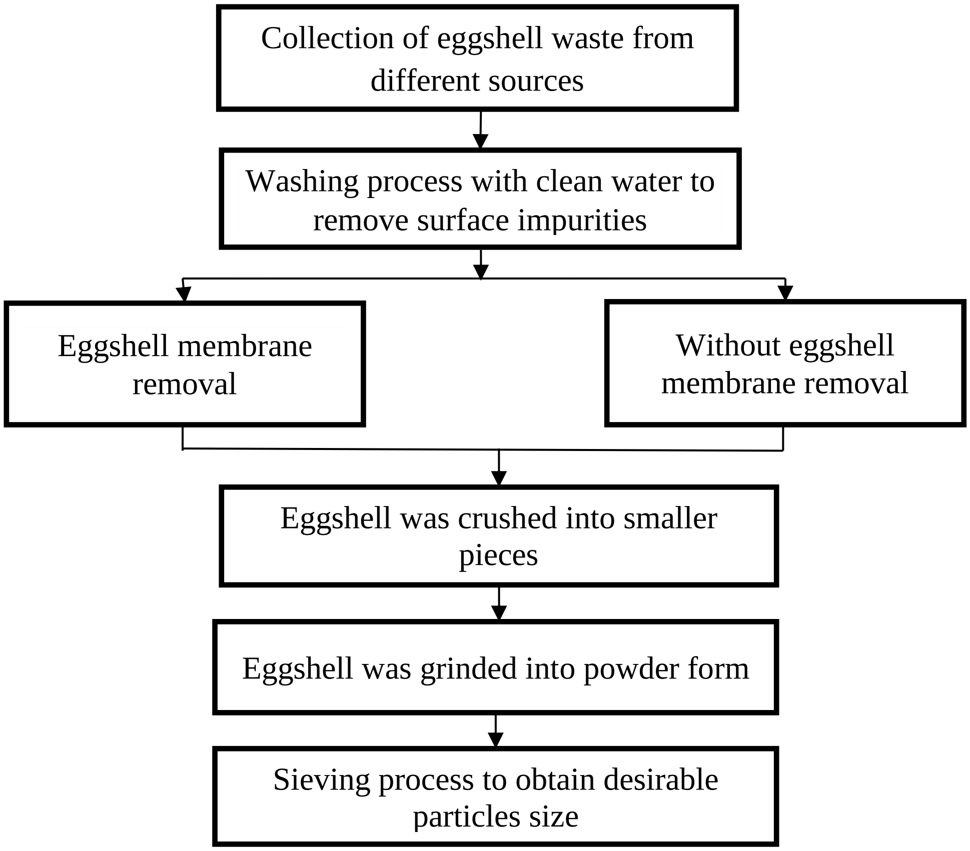


Figure 3.2: Schematic Diagram of Eggshell Based Calcium Carbonate powder Preparation.

3.4 Experiment Procedure

In this research study, SO_2 adsorption was performed in fixed bed reactor, with the constant parameters of dosage, flow rate, and SO_2 concentration. The process parameters are shown in **Table 3.3** below. The experiment system was performed in a furnace, where it consists of a tubular reactor inside of it, as well with a valves system and mass flow controllers in order to fix the desirable slow of composition of inlet gas (Zhu, et al., 2012). The compressed sulfur dioxide gas of 2000 ppm was diluted by nitrogen gas to obtain desired concentration of 300 ppm and absorbed by 1g of eggshell based calcium carbonate powder in this study. The 300 L/min of the gas flow rate was controlled by the nitrogen and sulfur dioxide mass flow meters. Before the mixing process, N_2 gas was passed over humidification process by submerging the cylinder flasks with water into thermostatic bath. The relative humidity (RH) of 40% were calculated based on **Eq 3.1**. The result of calculated RH is shown in **Table 3.4.**

Table 3.3: Adsorption Process Parameters

Adsorption studies	Parameters	Remark
Flow rate	300 mL/ min	Constant
Dosage of adsorbents	1g	Constant
Sulfur dioxide concentration	300 ppm	Constant
Relative Humidity (RH)	Without humidity, 40%	Variable
Reactor temperature	Room temperature, 100 °C	Variable
Particle size of eggshell powder	<180 µm, <125 µm, <90 µm	Variable

$$Relative\ Humidity\ (RH),\ \% = \frac{Partial\ Pressure\ of\ vapor\ (water\ bath\ temp.)}{Vapor\ Pressure\ of\ water\ (temp. of\ oven)}\ \text{X}100\% \qquad (3.1)$$

Table 3.4: RH Calculated Based on Reactor Temperature 100 °C

RH. (%)	Reactor Temp. (°C)	Water Bath Temp. (°C)	Partial Pressure of vapor (atm.)	Vapor pressure of water (atm.)
40	100	76	0.39664	1.0000

To ensure well-mixing of the gas, the N_2 gas and SO_2 gas were undergone bypassing process before flow through the reactor, where the initial concentration of SO_2 gas was measured by feeding the gas mixture to the coulometer. To observe the absorption capacity of eggshell based calcium carbonate powder, the SO_2 gas was tested under different parameters, including different temperature, different relative humidity and different particle sizes as shown in **Table 3.3**. The fixed-bed reactor with 180 mm height and 9 mm inner diameter was held with 1g of eggshell based calcium carbonate powder with different particle sizes: <180 µm, <125 µm and <90 µm. Before detected by the gas analyzer (Vario Plus Industrial Gas Analyzer, V:1.78-000, USA), the flue gas with different temperature condition (room temperature and 100^{o} C) was passing through a silica gel filter to absorb the moisture content of the flue gas.

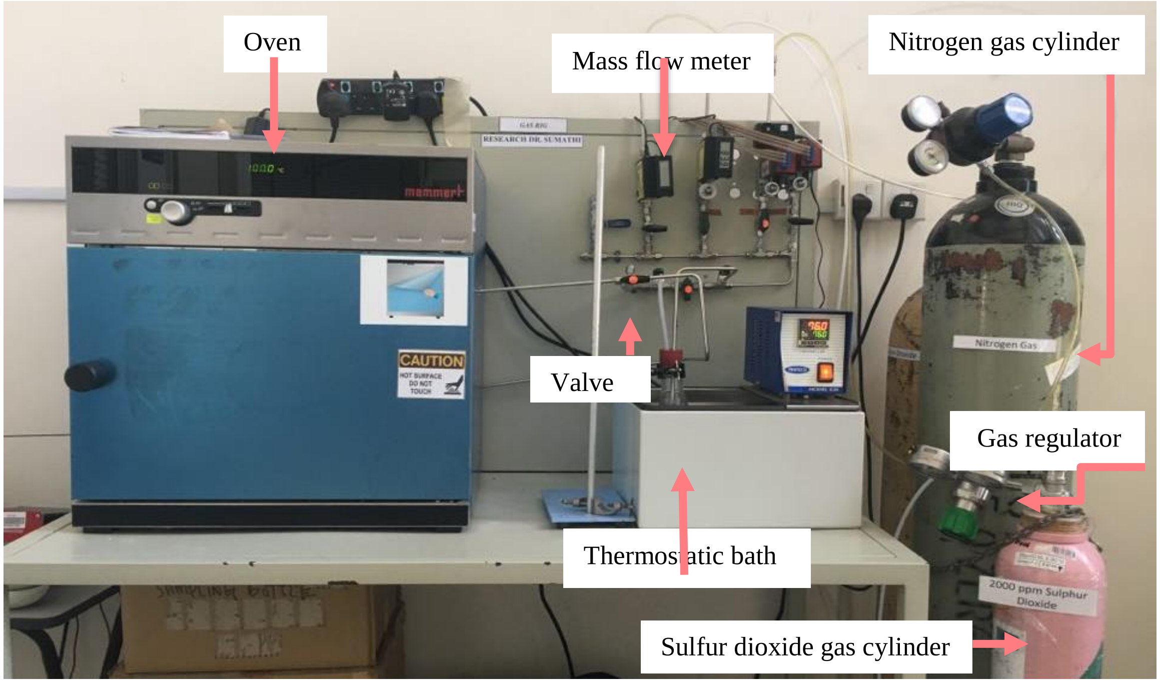
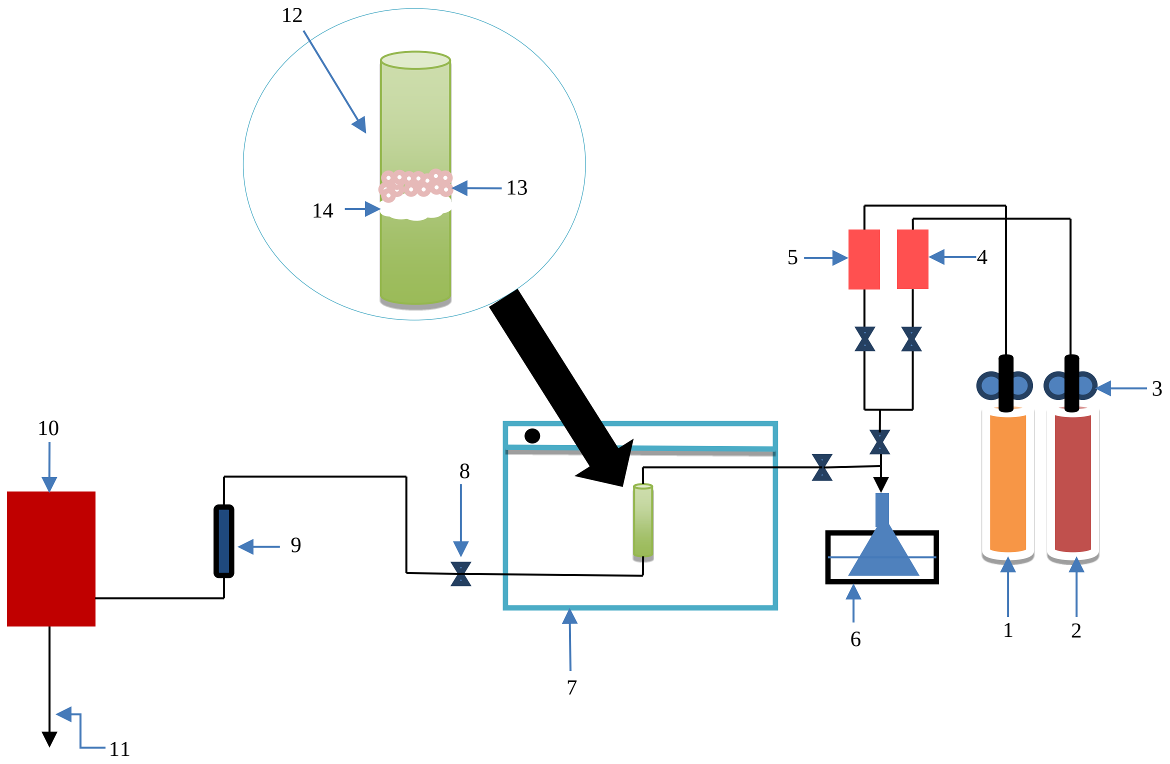


Figure 3.3: Experimental Setup of Sulfur Dioxide Gas Adsorption



Remarks:

1. Nitrogen gas cylinder
2. Sulfur dioxide gas cylinder
3. Gas regulator
4. Nitrogen gas flow meter
5. Sulfur dioxide gas flow meter
6. Water bath
7. Oven
8. Valve
9. Silica gel filter
10. Gas analyzer
11. Vent
12. Fixed-bed reactor
13. Adsorbent sample
14. Glass wool

Figure 3.4: Schematic Diagram of Sulfur Dioxide Adsorption Process Experimental Setup

3.5 Eggshell Based Calcium Carbonate Powder Characterization

The characterization of eggshell powder was done by several analysis, which included Fourier Transform Infrared Spectroscopy (FTIR) analysis, Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray spectroscopy (EDS) study.

3.5.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectroscopy is used to analysis structural information and a relevant composition of concerning samples (Mecozzi, et al, 2009). The functional groups on the surface of particular adsorbent can be identified by conducting FTIR spectroscopy analysis. The infrared spectroscopy always produce qualitative analysis of each kind of material, where the amount of the material can be indicated by the size of the peaks in spectrum (Thermo Nicolet Corporation, 2001). FTIR spectrometry has the advantages of measuring the infrared frequencies simultaneously, and is allowed most of the measurements done in a matter of seconds (Thermo Nicolet, 2001). Apart from high speed data collection of FTIR spectroscopy analysis, it also produces higher resolution, lower detection limits and higher energy throughput (Kemfert, et al., 2001).

3.5.2 Scanning Electron Microscopy (SEM)

SEM is common type of electron microscope which used to examine and analyze the microstructure morphology and the characterizations of chemical composition, proving higher resolution and greater depth of field compared with scanning confocal microscopes (Leng, 2008). The reasons make SEM is preferable in the study of solid materials as it is easy to operate and it requires minimal sample preparation (Susan, 2017). SEM is able to generate an image resolution better than the light microscope, which generally between 1 to 10 nm. A focused beam of high-energy electrons is used in SEM to produce a range of signals at solid sample's surface, and provide the sample information such as chemical structure, outer texture or morphology, and crystalline structure pattern and the materials' orientation (Susan, 2017). However, it serves some limitation as the tested samples must be in solid form, with the horizontal dimensions not beyond 10 cm, and vertical dimension less than 40 mm (Susan, 2017). Moreover, the very light elements such as hydrogen, helium and lithium cannot be detected by SEM. Since mostly a solid state X-ray detector is used in SEM, it tends to result poor energy resolution and sensitivity when the amount of elements are in low abundances (Susan, 2017).

3.6 Adsorption Capacity Calculation

The sulfur dioxide adsorption capacity can be calculated by the equation (3.2) below (Lau, et al., 2015):

$$Q = \frac{CoMw\,q}{1000w\,Vm}\int_0^t \left(1-\frac{C}{Co}\right)\,dt \qquad (3.2)$$

where

Q = adsorption capacity (mg SO_2/ g) of adsorbent,

c_o = the initial inlet concentration (ppm),

M_w = sulfur dioxide molecular weight (g/mol),

q = total flow rate (L/min),

w = the weight of adsorbent (g),

V_m = molar volume (L/mol),

c = the outlet concentration of sulfur dioxide (ppm) at time t (minutes).

Each set of experiment study was operated until it reached a saturation point where C/C_o is equal to 1.

CHAPTER 4

RESULT AND DISCUSSION

4.1 The Effect of Particle Size

The particle size of sample in powder form plays a vital role in the adsorption capacity of sulfur dioxide gas. In this research, the effects of different particle size: 90 μm, 125 μm and 180 μm towards the adsorption capacity of sulfur dioxide were observed and evaluated. To investigate the effects of different particle sizes, other parameters such as flow rate (300 mL/min), gas concentration (300 ppm), gas pressure (1 bar), temperature (ambient temperature), and without relative humidity (RH) were kept constant. **Figure 4.1** shows SO_2 breakthrough curve with different particle sizes versus two types of eggshell-based adsorbents i.e. *eggshell with membrane (ESM) and eggshell without membrane (ES).* The adsorption capacity of the eggshell-based adsorbents was further compared with the commercial calcium carbonate (CCC). The SO_2 removal capacities and the saturation for different particle size of ESM and ES are listed in **Table 4.1** along with the removal capacity of CCC.

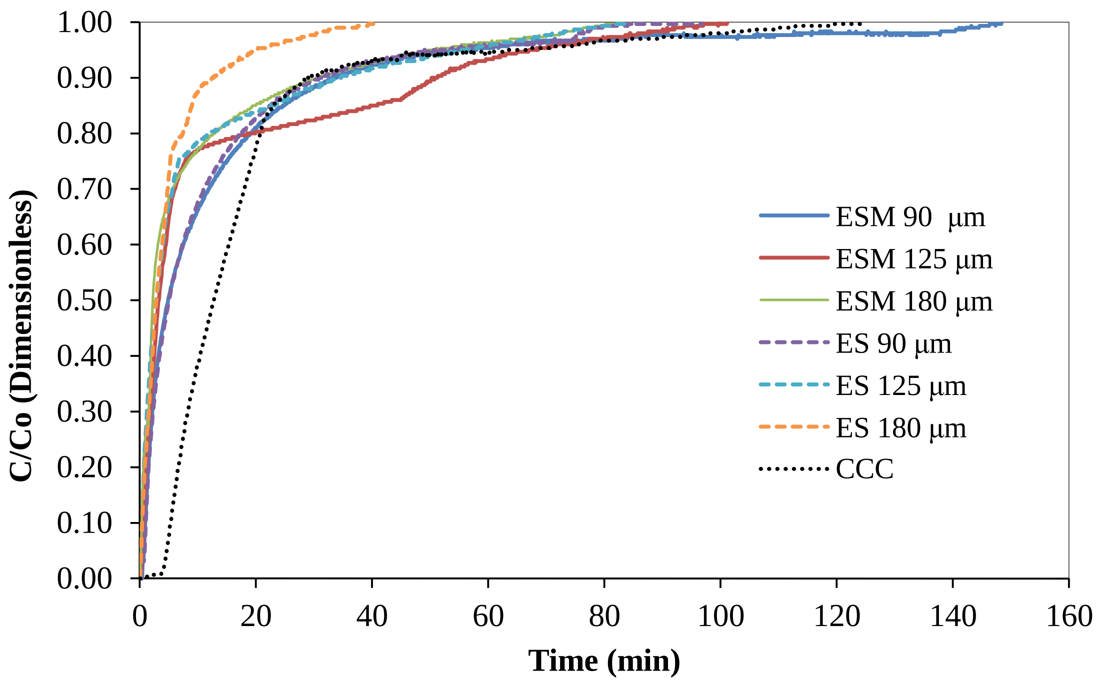


Figure 4.1: Breakthrough Curve on the Effect of Particle Size of ESM and ES Compared with CCC

Table 4.1: Sulfur Dioxide Adsorption Capacity Based on the Effect of Particle Size

Sample	**Saturation Time (min)**	**Adsorption Capacity (mg/g)**
ESM 180 μm	83.00	2.1950
ES 180 μm	41.25	1.1861
ESM 125 μm	95.33	3.1500
ES 125 μm	83.75	2.3314
ESM 90 μm	148.42	3.2100
ES 90 μm	96.75	2.7645
CCC	125.00	4.1459

Figure 4.1 shows that the adsorption rate for all types of samples increased faster at the first 10 to 20 min and started to slow down after the adsorption efficiency had reached about 75 to 80%. As displays in **Figure 4.1**, the ES 180 μm sample had the lowest adsorption capacity (1.1861 mg/g) and the shortest saturation time (41.25 min) whilst ESM 90 μm exhibited the best adsorption capacity (3.2100 mg/g) among the eggshell-based samples. Identical result was noticed for both ES and ESM samples in terms of particle size. The smallest particle size samples gave the highest adsorption capacity. The sequences from the highest adsorption capacity to the lowest adsorption capacity for EMS and ES are 180 μm > 125 μm > 90 μm. It should be noted that the smallest particle size had the longest saturation time. This indirectly show that, smaller particle size requires longer time to entirely lose its adsorption capacity. The reaction of sulfur dioxide gas on calcium carbonate can be illustrated by the chemical equation below (Al-Hosney and Grassian, 2005):

$$CaCO_{3\,(s)} + SO_{2\,(s)} \rightarrow CaSO_{3\,(s)} + CO_{2\,(g)} \qquad (4.1)$$

However, the reaction mechanism between calcium carbonate and sulfur dioxide gas has slightly different when the temperature more than 750 K as illustrated below (Al-Hosney and Grassian, 2005):

$$CaCO_{3\,(s)} + SO_2 + \tfrac{1}{2}\,O_2 \rightarrow CaSO_{4\,(s)} + CO_{2\,(g)} \qquad (4.2)$$

Based on the research done by Karatepe, et al. (2008), it was stated that when the inlet concentration of sulfur dioxide gas was decreased and the sample particle size was increased, the amount of sulfur dioxide adsorbed was significantly decreased. For instance, the study of Karatepe, et al. (2008) proved that with the particle size ranged from 100-150 μm and 500-600 μm, the former particle size showed better SO_2 uptake than the latter sample under different inlet gas concentration. Moreover, it was reported that the SO_2 adsorption capacity is greatly affected by some textural properties such as pore volumes, surface area and pore size distribution (Karatepe, et al., 2008). Witoon (2011) had reported that the smaller particle size calcined eggshell particles have higher CO_2

capture capacity as it provides higher exposed surface for the surface reaction of CO_2. Furthermore, it is evidence that smaller particle size has higher weight loss, surface area and more developed micropore volume (Li, Kobayashi and Hu, 2008). Smaller particles also tend to offer more surface area for the gas-solid reaction, and thus have higher desulfurization rate (Zhai, et al., 2017). However, due to the heterogeneous characteristic of the sample's surface, there is no certain relationships between the surface functional groups, textural properties and SO_2 adsorption (Karatepe, et al., 2008). Moreover, Witoon (2011) stated the pore characteristics for the dried eggshell sample showing no multilayer gas adsorption, and indicated the sample only consisted macropore. The pores and pits irregularly distributed over the surface of the dried eggshell (Witoon, 2011) is believed one of the major factors on causing low adsorption capacity in this study.

In the aspect of the adsorbent types, the ESM samples displayed better performance than the ES samples. In **Table 4.1**, ESM samples performed higher adsorption capacity compared to ES samples. Therefore, it can be concluded that eggshell membrane can be used to enhance SO_2 adsorption process. Several literature had also reported that eggshell membrane had been proven as a potential sorbent for different substances such as metals, phenol, and dyes (Al-Ghouti and Khan, 2017). According to Tsai, et al., 2006, eggshell membrane consists of a network of fibrous proteins and it has a larger surface area compared to ES. Despite there is no literature review on the effect of eggshell membrane on gas adsorption, Pramanpol and Nitayapat (2006) reported that eggshell membrane has a better adsorption capacity and, possibly, adsorption affinity for the reactive dye compared to the eggshell. Besides, Gregg and Sing (1982) also determined that the pore structure of these two eggshell-based adsorbents are categorised as Type II according to Brunauer, Deming, Deming and Teller classification, specifying their basic characteristic either belong to nonporous materials, macropores materials or materials with open voids. It was also stated that the BET surface of the eggshell membrane is larger than the eggshell (Tsai, et al., 2006), possibly leads to the better adsorption capacity in this case. Moreover, the density of ESM was reported as 2.532 g/cm^{-3} by Tsai, et al. (2006), where the density of calcite is 2.710 g/cm^{-3}, indicated that the major component of eggshell is calcium carbonate in the form of calcite.

In addition, the comparative studies with the ESM, ES and CCC had been done in this research study. As shown in **Figure 4.1** and **Table 4.1**, the adsorption capacity of CCC is 4.1459 mg/g, is higher compared to the optimum result found for ESM 90 µm (3.2083 mg/g). The lower adsorption capacity of the ESM compared to CCC is mainly due to the eggshell properties. According to Soares, Quina and Quinta-Ferreira (2015), 100g of air-dried of eggshell waste equivalent to 88 g of $CaCO_3$. Another literature done by Sethupathi, et al. (2017) found that the eggshell BET surface area was 0.56 m^2/ g and the CCC BET surface area was 1.12 m^2/ g. This explains well the CCC always had the better adsorption performance than the eggshell-based adsorbents due to the higher BET surface area. Moreover, CCC used in this study is 99% pure with analytical grade and this could be a strong reason that CCC to perform better compared to ESM.

4.2 The Effect of Temperature

The influence of the temperature to the SO_2 adsorption was studied and investigated under the condition of 300 mL/min of gas flow rate, 1g of adsorbent dosage, 300 ppm of SO_2 concentration, and 1 bar of gas pressure. The optimized adsorbents chosen from the previous section was chosen to study the effect of temperature. ESM 90 µm, ESM 180 µm, and CCC were chosen. It should be noted that the effects of temperature to the largest and smallest particle size were evaluated. Therefore, the particle size of 125 µm was neglected in studying the temperature effect is due to its moderate adsorption capacity.

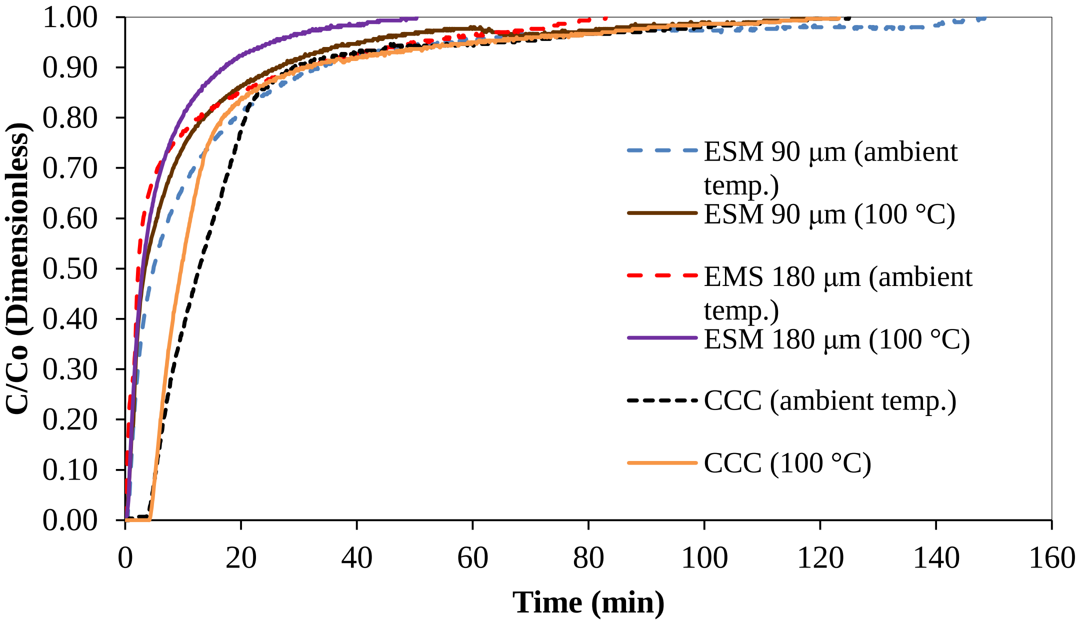


Figure 4.2: Breakthrough Curve on the Effect of Temperature to ESM and CCC Adsorption Capacity

Table 4.2: Sulfur Dioxide Adsorption Capacity Based on the Effect of Temperature

Sample	**Temperature (°C)**	**Saturation Time (min)**	**Adsorption Capacity (mg/g)**
ESM 90 µm	Ambient temperature	148.42	3.2100
ESM 90 µm	100	119.42	2.3749
ESM 180 µm	Ambient temperature	83.00	2.1939
ESM 180 µm	100	41.25	1.1861
CCC	Ambient temperature	125.00	4.1459
CCC	100	123.25	3.7033

To investigate and evaluate the capacity of sulfur dioxide removal, the adsorption test was studied at ambient temperature and 100 °C of reactor temperature. According to the results shown in **Figure 4.2**, ambient temperature, CCC showed the best SO_2 adsorption capacity, which is 4.1459 mg SO_2/g with 125 min of saturation time. From the results obtained, it can be clearly seen that the adsorption capacity of adsorbents decrease with the increase of temperature. The adsorbents of EMS 90 µm, ESM 180 µm and CCC at ambient temperature had better adsorption capacity than at 100 ^{o}C. At ambient temperature, ESM 90 µm adsorption capacity was 3.2100 mg/g, and decreased to 2.3749 mg/g when the temperature was increased to 100 ^{o}C. Similar result was obtained for ESM 180 µm and CCC, where the adsorption capacities of ESM 180 µm and CCC decreased to 1.1861 mg/g and 3.7033 mg/g, respectively. It can also be concluded that at ambient temperature, sulfur dioxide adsorption process is more favourable.

The effects of temperature ranged from ambient temperature to 100 ^{o}C on SO_2 adsorption were not clearly identified and there is very little information on it. However, this result was supported by the finding of Karatepe, et al. (2008), where the amounts of SO_2 adsorbed reduced when the adsorption temperature increased. This is due to the reason that the SO_2 molecules lose their kinetic energies during the adsorption process, causing the process became exothermic (Cheng and Harriott, 1986; Lua and Guo, 2001). Similar finding was also proven by Hosseini, et al. (2017), where the CO_2 adsorption using calcined eggshell was decreasing at higher temperature. From 30 ^{o}C to 50 ^{o}C, the adsorbed amounts of CO_2 were found significantly decreased from 0.0928 to 0.0869 mmol/g (Hosseini, et al., 2017). This is assigned to the exothermic reaction of the process where the rate of molecular diffusion and the surface adsorption energy increase with the increasing of temperature (Guo and Lua, 2002; Maroto-Valer, et al., 2005). The exothermic reaction was indirectly causing less amount of SO_2 gas being absorbed into the pores of adsorbents (Sumathi, et al., 2014). For gas separation process, adsorption process is efficient at temperatures much lower than ambient temperature. However, the process is rather expensive. This is also one of the major reasons that adsorption process at room temperature is more preferable in industrial sector. For the adsorption at higher temperature, the loss of adsorption capacity can be balanced by using higher pressures, which commonly in the range of 5 to 150 bar (Rouquerol, Rouquerol and Sing, 2014).

It was claimed that rising in temperature is expected to have faster chemical reaction rate between H_2SO_3 and $CaCO_3$ or $Ca(OH)_2$ (Slack, Falkenberry and Harrington, 1972). When the temperature is increased, it was suggested that the adsorbate earns more thermal energy to subdue the wall potential, therefore, causing less adsorption happens at higher temperatures (Yi, et al., 2014). On the other hand, Wu, et al. (2011) also reported the formation rate of sulfate increased slowly at the beginning and then decreased with the decreasing of temperature (230-257K). It can be seen that the saturation time of eggshell-based adsorbent is longer at lower temperature. Wu, et al. (2011) explained that this scenario occurs when there is insufficient thermal energy for the reaction to overcome the activation energy and, it may require longer time to complete the overall reaction at low temperature. The studies done by Wu, et al. (2011) based on the heterogeneous oxidation of SO_2 by ozone on $CaCO_3$ explained that in the range of 298 to 250K, the sulfate formation rate increased with decrease of temperature, while this process reversed in the temperature range of 250 to 230K. It was also reported by some literature that different adsorbents perform their best adsorption capacity at different temperature. For instance, the SO_2 adsorption capacity of Y zeolite was observed decreases with the increase of temperature above 200 ^oC. (Marcu and Sandulescu, 2004), whereas 5A zeolite was found its maximum breakthrough time reached when the temperature ranged from 70-80 ^oC (Gupta, et al., 2004).

4.3 The Effect of Relative Humidity

SO_2 adsorption capacity was also studied and evaluated in the presence and absence of relative humidity. With the presence of 40% of relative humidity, the effects of adsorption capacity on ESM 90 μm and CCC were observed and compared with the results under the conditions of without relative humidity. The constant parameters were gas flow rate (300 mL/min), SO_2 concentration (300 ppm), adsorbent dosage (1g), gas pressure (1 bar), and temperature (100 ^oC). According to the previous results obtained, ESM 90 μm exhibited the highest adsorption capacity among the eggshell-based adsorbents, thus this sample was selected. The adsorption capacity corresponding to relative humidity was displays in **Figure 4.3**. The adsorption capacity results and saturation time were listed in **Table 4.3.**

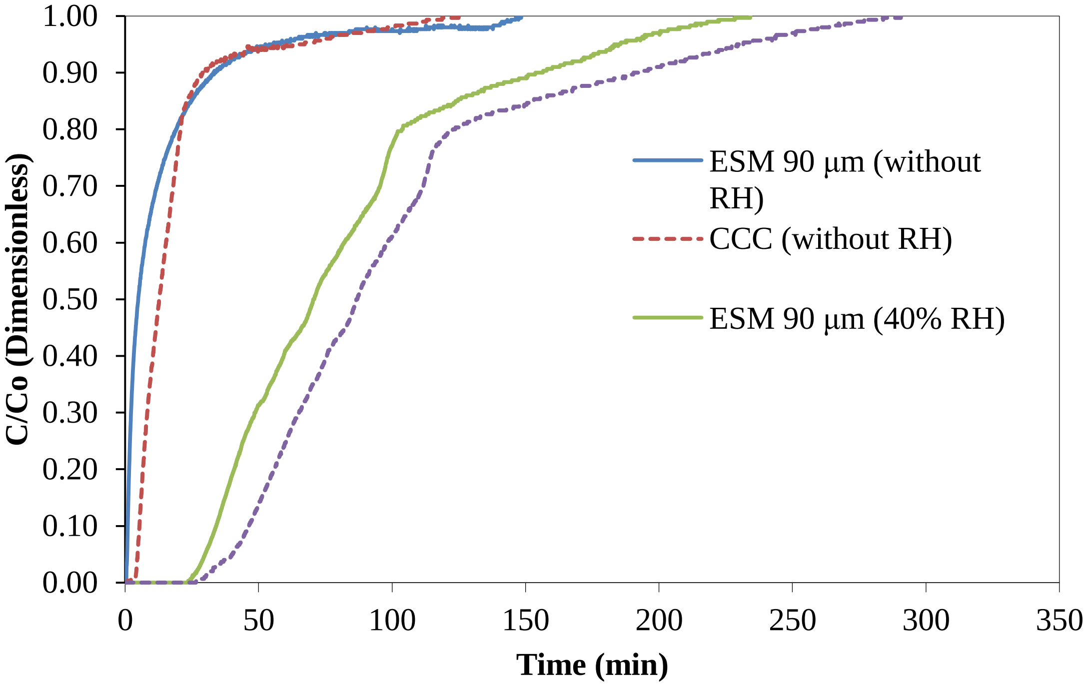


Figure 4.3: Breakthrough Curve on the Effect of Relative Humidity

Table 4.3: Sulfur Dioxide Adsorption Capacity Based on the Effect of Relative Humidity

Sample	**Relative Humidity (%)**	**Saturation Time (min)**	**Adsorption Capacity (mg/g)**
ESM 90 μm	Without	148.42	3.2100
ESM 90 μm	40	244.08	18.7472
CCC	Without	125.00	4.1459
CCC	40	290.67	23.2435

As presented in **Figure 4.3**, at RH of 40%, EMS and CCC had better performance compared to without RH. For ESM 90 μm, the adsorption capacity without RH and with 40% RH was recorded as 3.2100 mg/g and 18.7472 mg/g, respectively. In the other words, the adsorption capacity of ESM 90 μm increased up to 5.84 times in the presence of 40% RH. On the other hand, the adsorption capacity of CCC was increased from 4.1459 mg/g (without RH) to 23.2435 mg/g, which was approximately 5.6 times better than without RH. The adsorption performances can be sequenced as following CCC (40% RH) > ESM 90 μm (40% RH) > CCC (without RH) > ESM 90 μm (without RH). It is noted that at 40% RH, ESM 90 μm and CCC exhibited significant breakthrough times, *i.e. 23.50 min and 26.50 min, repectively.* The significant increase in breakthrough time was owning to the strong interaction of the gas molecules and the adsorbents (Nasri, et al., 2017).

Apart from that, time taken for the CCC and ESM to reach 80% of SO_2 removal are approximately 122 min and 112 min, respectively. Compared to the CCC and ESM under the same condition without introducing the relative humidity into the gas stream, the time taken to reach 80% of SO_2 removal are approximately 21 min and 19 min, respectively. The reaction of sulfur dioxide and calcium carbonate in the presence of relative humidity is different from previous reaction. Carbon dioxide is not a product in this reaction but the carboxylic acid (H_2CO_3) (Al-Hosney and Grassian, 2005). However, during the adsorption process CO_2 reading was noticed by the analyser. The chemical reaction is as shown as below:

$$CaCO_{3\,(s)} + H_2O\ (g) \rightarrow Ca(OH)(CO_3H) \tag{4.3}$$

$$Ca(OH)(CO_3H) + SO_{2\,(g)} \rightarrow CaSO_3 + H_2SO_3 \tag{4.4}$$

The $CaCO_3$ substrate surface with adsorbed water plays a vital role in the heterogeneous reaction with acidic trace gases such as sulfur dioxide (Santschi and Rossi, 2006). Literature has reported that water can improve the adsorption of atmospheric gases on carbonate and oxide minerals (Al-Hosney and Grassian, 2005). For instance, in humid air condition, the deposition velocity of sulfur dioxide gas had been increased on dolomite and calcite (Al-Hosney and Grassian, 2005). According to Ma, et al. (2012), water vapor had significant effect on desulfurization, where SO_2 adsorption capacity can be improved by increasing the water vapor content. The SO_2 will first be oxidized to SO_3, then become sulfuric acid when water vapor had been introduced into the gas stream (Ma, et al., 2012). A research by Sitthikhankaew, et al. (2014) found that in the presence of relative humidity, the H_2S adsorption performance can be improved and the adsorption capacity can be increased.

Based on the research done by Ruiz-Alsop and Rochelle (1988), it was proved that at higher relative humidity, the reaction rate of SO_2 removal decreased more slowly than the lower relative humidity the fast reaction at the beginning. Li, et al. (2009) claimed that relative humidity can affect both the reaction mechanism and the initial uptake coefficient. The reaction order is determined by the formation of surface —OH through the dissociation of the $CaCO_3$ surface adsorbed water via oxygen vacancy under the condition of low RH (Li, et al., 2009). The dissociation of water was demonstrated to produce surface hydroxyl on $CaCO_3$ surface (Kuriyavar, et al., 2000; Stipp, 1999). The water condensation process as well starts on the surface as RH increase, and the gas-solid reaction will change to gas-liquid reaction (Li, et al., 2009; Li, et al., 2010). Similar study had been conducted by Li, et al. (2010) and has concluded that at low RH, there will be a competition between water and NO_2 for the —OH active sites which decrease the uptake coefficient. However, as RH increases, water condensation occurs on the surface of $CaCO_3$ particles, causing the formation of micro-puddles of water, and the gas (NO_2)-liquid reaction may become feasible (Li, et al., 2010). Therefore, it was concluded the mechanism of heterogeneous reactions are greatly influenced by water.

Water layer which is present on the adsorbent can alter the structure and composition of the interface, therefore it plays an important role on the chemistry reaction of particles and single crystals surfaces with NO_2, SO_2, CO_2, O_3 and organic acids (Rubasinghege and Grassian, 2013). Between 30% and 85% RH, sulfur dioxide and calcium carbonate reaction is enhanced significantly, approximately to 5 to 10 fold for particulate and single crystal $CaCO_3$ (calcite) in the presence of adsorbed water (Baltrusaitis, Usher and Grassian, 2007). It was also reported that the adsorbed water can enhance the mobility of surface ions, causing the formation of nanometer sized product crystallites about 1 nm height and also pitting and etching of the underlying substrate (Baltrusaitis, Usher and Grassian, 2007). In the absence of water, the formation of crystallites shows no evidence, and there is only little pitting can be found (Rubasinghege and Grassian, 2013). Therefore, it was suggested that the adsorbed water to calcium carbonate surface not only can enhance the ion mobility, it also permits the SO_2 hydrolysis reaction to produce H_2SO_3 (Rubasinghege and Grassian, 2013). Apart from that, it was suggested that in the presence of adsorbed water, the reaction of dissolution recrystallization can offer extra surface sites for the chemical reaction to continue (Rubasinghege and Grassian, 2013).

4.4 Characterisation

4.4.1 Functional Group Analysis

Chemical structures of sample’s surface are another factor influencing the adsorption capacity. As the sample might contain unpaired electrons, incompletely saturated valances and/ or certain functional groups, the surface attraction force and also adsorption capacity will be undoubtedly affected (Karatepe, et al., 2008). Fourier Transform Infrared Spectroscopy (FTIR) test was carried out to identify chemical constituents of the ECC. It is a useful method to determine the infrared spectrum of sample absorption (Krumins, Klavins and Seglins, 2012). By comparing the standard frequency patterns of spectra, different stretching or chemical bonds were identified, and from which to determine certain functional groups (Karatepe, et al., 2008). The chemical structures of the sample structure play a vital role as they tend to influence the adsorptive capacity (Karatepe, et al., 2008). The presence of any unpaired electrons, incompletely saturated valances and/ or certain functional group will affect the surface attraction force and eventually the adsorption capacity (Karatepe, et al., 2008). The functional group present on the sample's surface will greatly affect the adsorption characteristics. All spectra were analysed in the infrared region of 400 to 4000 cm^{-1}. **Figure 4.4** shows FTIR spectra of ES, ESM and CCC before adsorption.

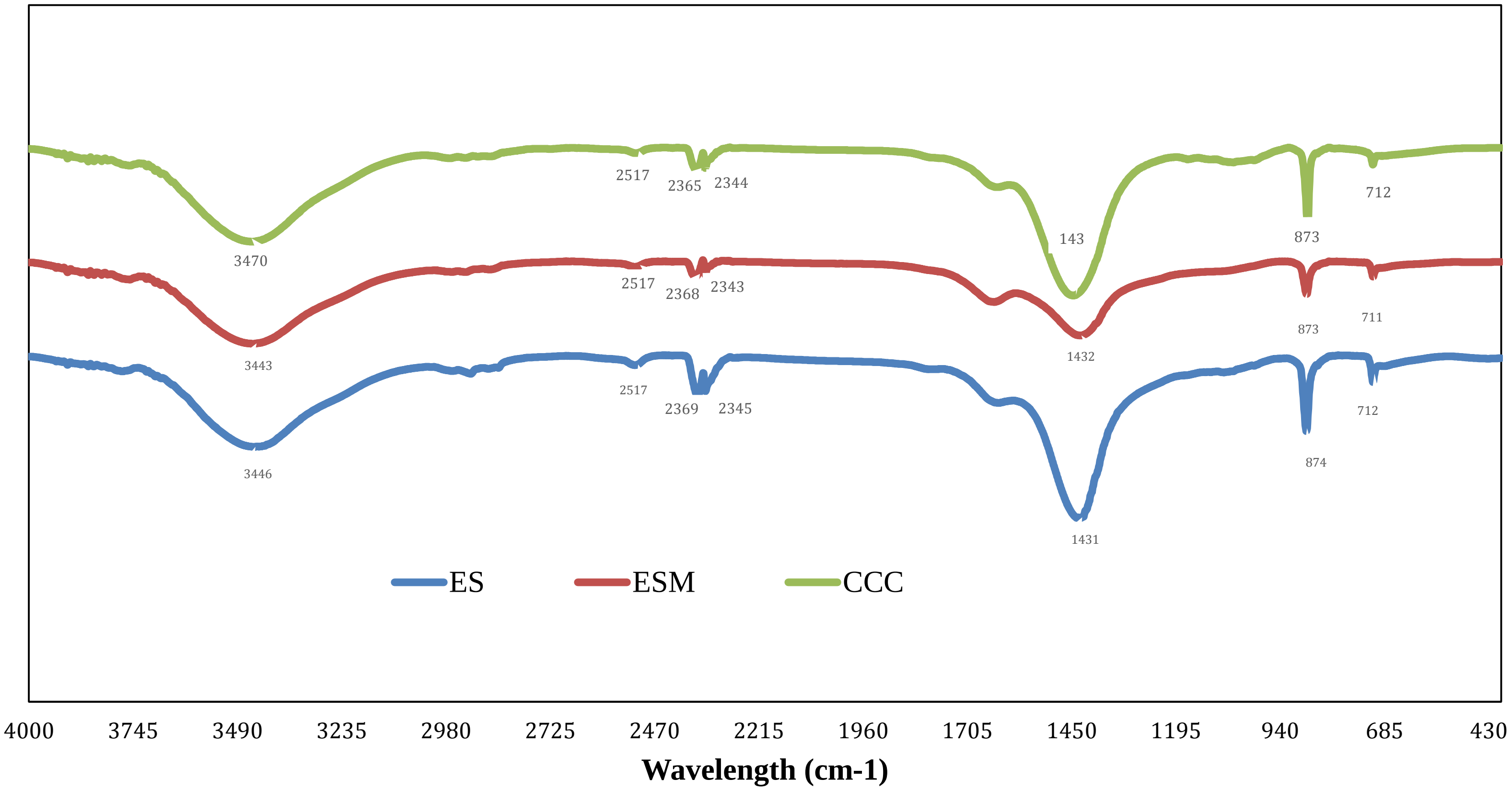


Figure 4.4: FTIR Spectra of ES, ESM and CCC before Adsorption Performance

Based on **Figure 4.4**, it is clearly seen that all samples exhibited similar infrared (IR) spectra. The broad bands found at 3470, 3443 and 3445 cm^{-1} were assigned to hydrogen-bonded OH groups as it was exhibited between the spectrum region between 3300-3670 cm^{-1} (Krumins, Klavins and Seglins, 2012; Li, etc., 2013). Similar result was obtained by Elkady, Ibrahim and El-Latif (2011), where 3432.13 cm^{-1} spectrum was found in the eggshell composite, indicating the stretch vibration of O—H. Reported by Witoon (2011), similar peak was found at 3428 cm^{-1} in the eggshell composite where it was assigned to OH stretching vibration. Besides, there is a peak found in the range between 2918 and 2920 cm^{-1} for the three adsorbents, which falls in the region between 2850-2950 cm^{-1}, indicates the presence of aliphatic C-H, $C\text{-}H_2$, $C\text{-}H_3$ stretching (Krumins, Klavins and Seglins, 2012). Another sharp band at 2364 cm^{-1} can be assigned to the stretching vibration of OH group (Colovic, Jokanovic and Jovic, 2013; Singare, Lokhande and Madyal, 2011). The spectrum at 2345 cm^{-1} peak was assigned to the asymmetrical stretch of CO_2 molecule (Li and Sun, 1997; Glascoe, et al., 2009; Goodman, Underwood and Grassian, 2000). The 2517 cm^{-1} peak represents stretching C-OH as the spectrum falls in the region between 2500-3620 cm^{-1} (Madzaki, et al., 2016). The results obtained above indicated the presence of carboxyl, amino, and hydroxyl groups (Park, et al., 2016).

Moreover, the graph also showed a peak at 1425 cm^{-1}, which can be assigned to C-N stretching-in-plane OH bending (Gokulakumar and Narayanaswamy, 2008; Shi, Xing and Li, 2012). There is hydrogen-bonded OH stretching of carboxylic groups found between the region of 750-880 cm^{-1}, where it was found at 873 and 874 cm^{-1} in the graph shown in **Figure 4.4** (Krumins, Klavins and Seglins, 2012). The statement is supported by Goodman, Underwood and Grassian (2000), where the negative 875 cm^{-1} band is assigned to the out-of-plane bend of $CaCO_3$, and indicated the loss of carbonate. Based on Reig, et al. (2002) research, the spectrum of 712 cm^{-1} indicates the presence of calcite and this finding is supported by Ramachandran and Beaudoin (2001) and Pyrzynski, Nyszko and Zaikov (2016), which the band at 712 cm^{-1} was assigned to carbonate bands, showing the sample particle was strongly attached with the presence of carbonate materials. Same peak value was found in Witoon's research (2011), where it was reported that 712 cm^{-1} sharp peak detected in dried eggshell, attributed to Ca-O bonds.

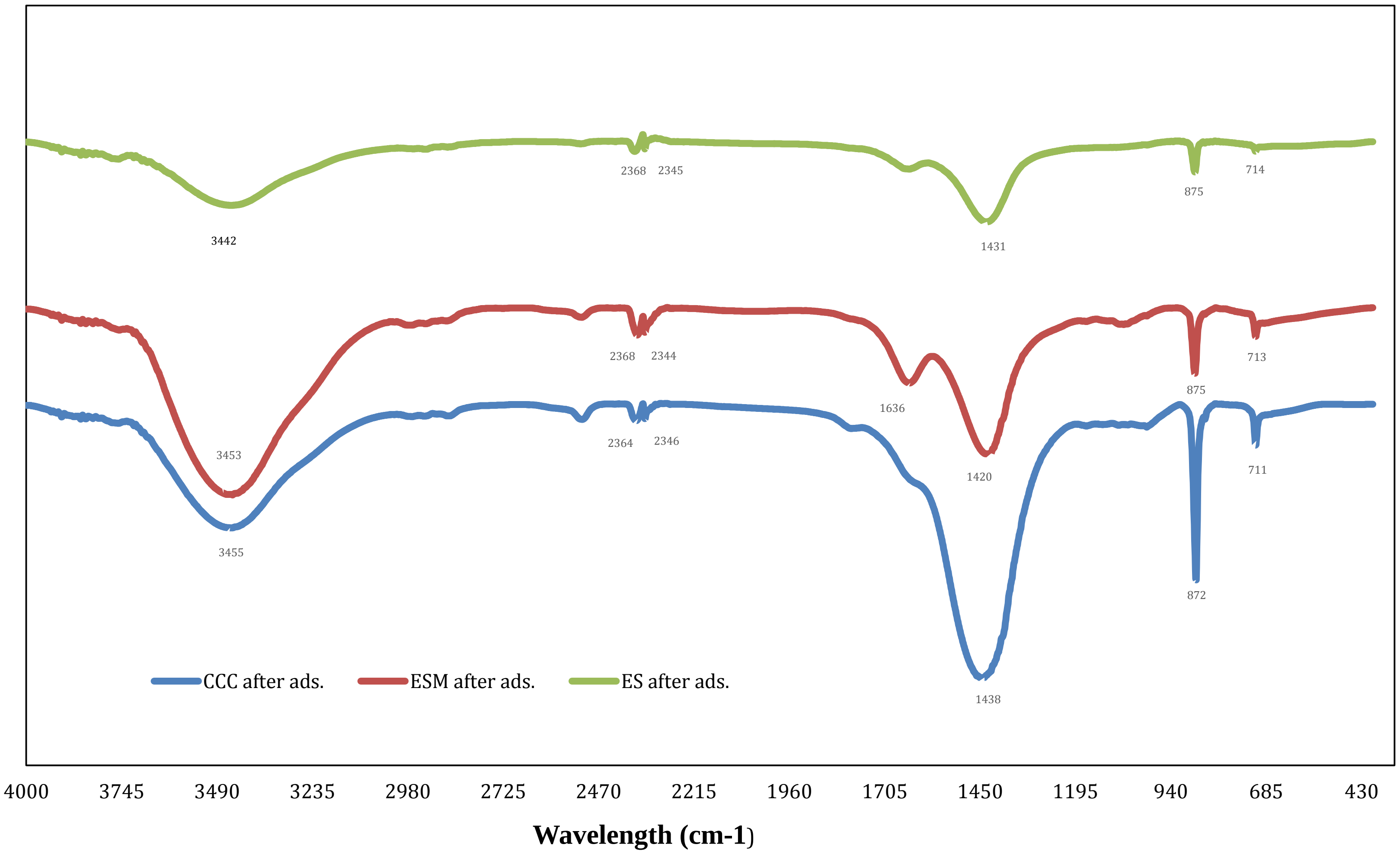


Figure 4.5: FTIR Spectra of CCC, ESM, ES after SO_2 Adsorption (Ambient Temperature, Without Relative Humidity)

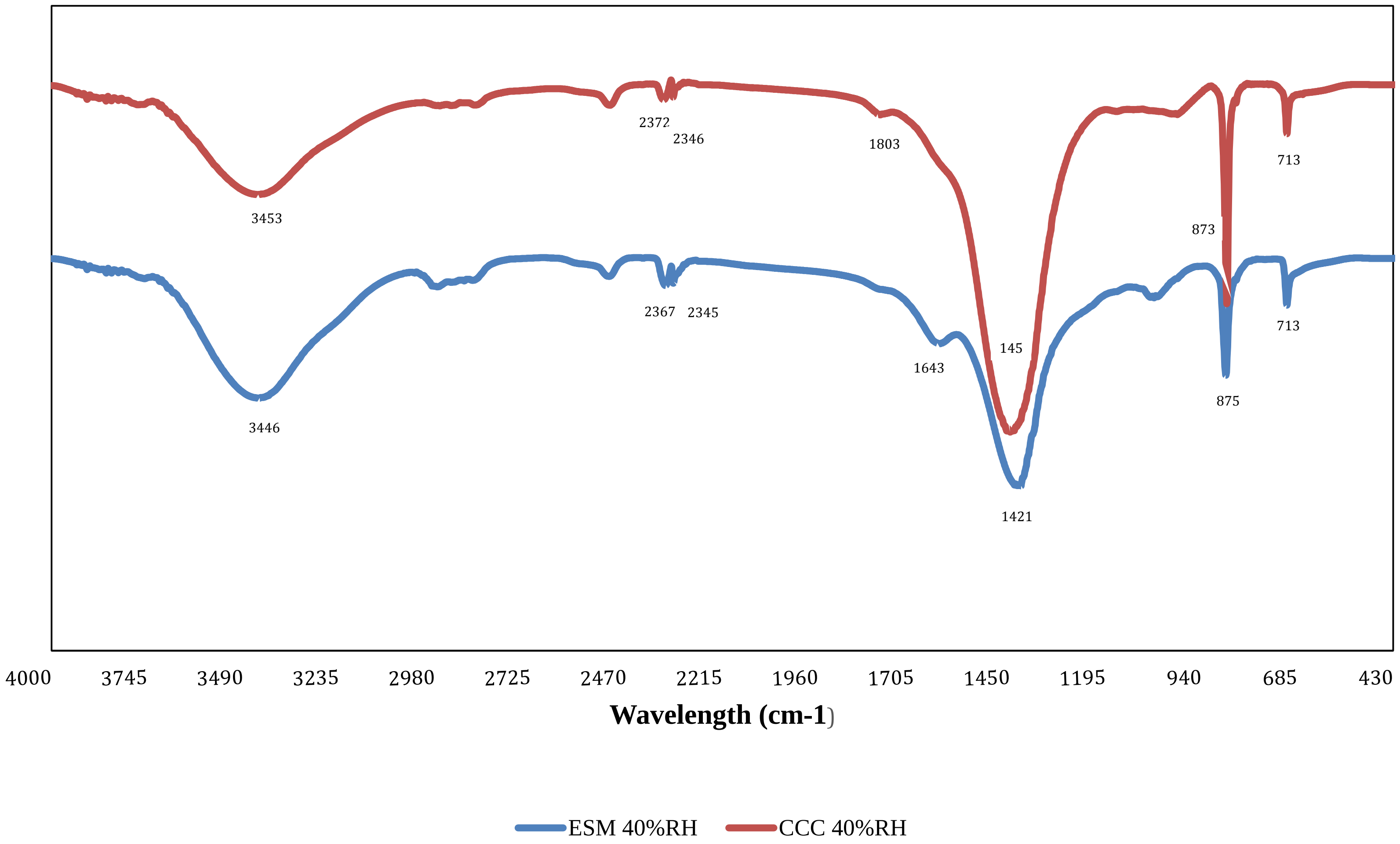


Figure 4.6: FTIR Spectra of CCC and ESM with 40%RH after SO_2 Adsorption at 100 °C

Figure 4.5 shows the FTIR spectra of all the adsorbents after the SO_2 removal process whereas **Figure 4.6** shows the FTIR spectra for SO_2 adsorption process using ESM 90 µm and CCC at 40% RH and 100 ^oC. From the results exhibited, similar functional groups with the adsorbents before SO_2 removal process were observed. Extra peaks had been detected by FTIR for the ESM with 40% RH at 100 ^oC oven temperature and ESM after adsorption process. The IR 1643 cm^{-1} and 1636 cm^{-1} spectra is attributed to the stretching vibration of carbonyl group characteristic of secondary amides and other compounds consisting C=O group (Ramamurthy and Kannan, 2007). Similar result was found in the study of Flores-Cano, et al. (2013), where the spectrum at 1645 cm^{-1} found in eggshell was attributed to bending vibration in primary amines (N-H). According to Tsai, et al. (2006), similar peak (1651 cm^{-1}) was found in eggshell membrane particles, which indicated the presences of amines and amides. This band also assigned to the bending mode of water molecules that are adsorbed on the sample's surface (El-aziz, El-Maghraby and Taha, 2016; Rubasinghege and Grassina, 2013). Apart from that, another weak peak was observed in 1803 cm^{-1}, which can be attributed to the C=O bonds from carbonate according to the publication of Witoon (2011) as similar spectrum (1795 cm^{-1}) had been detected in calcined commercially available $CaCO_3$.

4.4.2 Surface Morphology and Physical Properties

To identify and characterize the surface morphology and the physical properties of eggshell-based adsorbents, scanning electron microscopy (SEM) is a very essential method to use (Al-Ghouti and Khan, 2018). The elemental analysis had been performed for the ESM and ES adsorbents using energy dispersive X-ray spectroscopy (EDS). SEM analysis was performed to study the surface morphology, shape and size of ESM and ES. **Figure 4.7** presents the images of SEM at 10,000 magnification. ESM's SEM image exhibited irregular surface structure and identical results alike research done by Al-Ghouti and Salih (2018). **Figure 4.7** shows clearly the presence of eggshell membrane, a complicated matrix of protein fibers interconnected with each other (Flores-Cano, et al., 2013). Moreover, **Figure 4.7** displays the ESM surface with irregular crystal textural structure, and this identical structure finding had been proved in the research study done by Kose and Kivanc (2011). Pores and pits with different sizes distributed on the surface of ESM (Witoon, 2011). It was also reported that the eggshell membrane particle had the rod-like-fibrous-fractures shape (Yang, et al., 2003) which can be seen in **Figure 4.7 (a)**.

Moreover, when SEM image of ESM adsorbent was observed, the result exhibited irregular clumped structure, where identical SEM results were reported by Al-Ghouti and Salih (2018). Compared to the calcined eggshell structure published in other literature, ESM had less developed pore structure, which can affect the sulfur dioxide adsorption performance in this study. It was also reported that the pore size of ESM is range from 0.3 to 0.6 µm (Arunlertaree, et al., 2007). Apart from that, large blocky crystal was reported to form after the SO_2 removal process, where the $CaSO_4$. $2H_2O$ was started to form (Slack, Falkenberry and Harrington, 1972). After adsorption process with 40% RH, the surface layer of ESM. Comparing to the smooth surface of the ESM before SO_2 adsorption process, the surface layer of ESM after the SO_2 adsorption process become eroded and roughened, indicating the formation of $CaSO_3$ (Rubasinghege and Grassian, 2013).

EDS spectra which exhibited in **Figure 4.7(b)** below had been proved with the presence of C, Ca, O, and Mg component in ESM. Similar eggshell composition except phosphorus had been found and proved by the research of Gao and Xu (2012), where all these constituents had been found in their EDS analysis. Besides, the EDS also showed with the presence of S component after the adsorption process, where two new S component spectra were identified. Apart from that, the peak attributed to Ca component becomes less significant after the SO_2 removal activity. This result indicated that after the SO_2 adsorption process, the calcium component becomes lesser and the sulfur component had been introduced to the adsorbent. Besides, the weight percentage of C component in ESM shows in **Table 4.4** had been increased after the adsorption process. According to He, et al. (2017) and Witoon (2011), it was evidenced that eggshell CaO-based sorbents could be used to capture the CO_2 gas. The weight percentage increment of C composition after the adsorption performance proved the presence of carbon dioxide in the gas stream during the SO_2 adsorption process. Therefore, it is believed carbon dioxide is one of the factors that can affect the SO_2 removal efficiency. Apart from that, carbon dioxide is one of the production of the reaction of SO_2 gas on $CaCO_3$ (Al-Hosney and Grassian, 2005), which supporting the reason of the presence of C component. According to the literature of Tsai, et al. (2006), the eggshell with membrane should consist of N component, which could not be detected by the EDS analysis. The reason might be the amount of N component is too minor which is hard to be analysed.

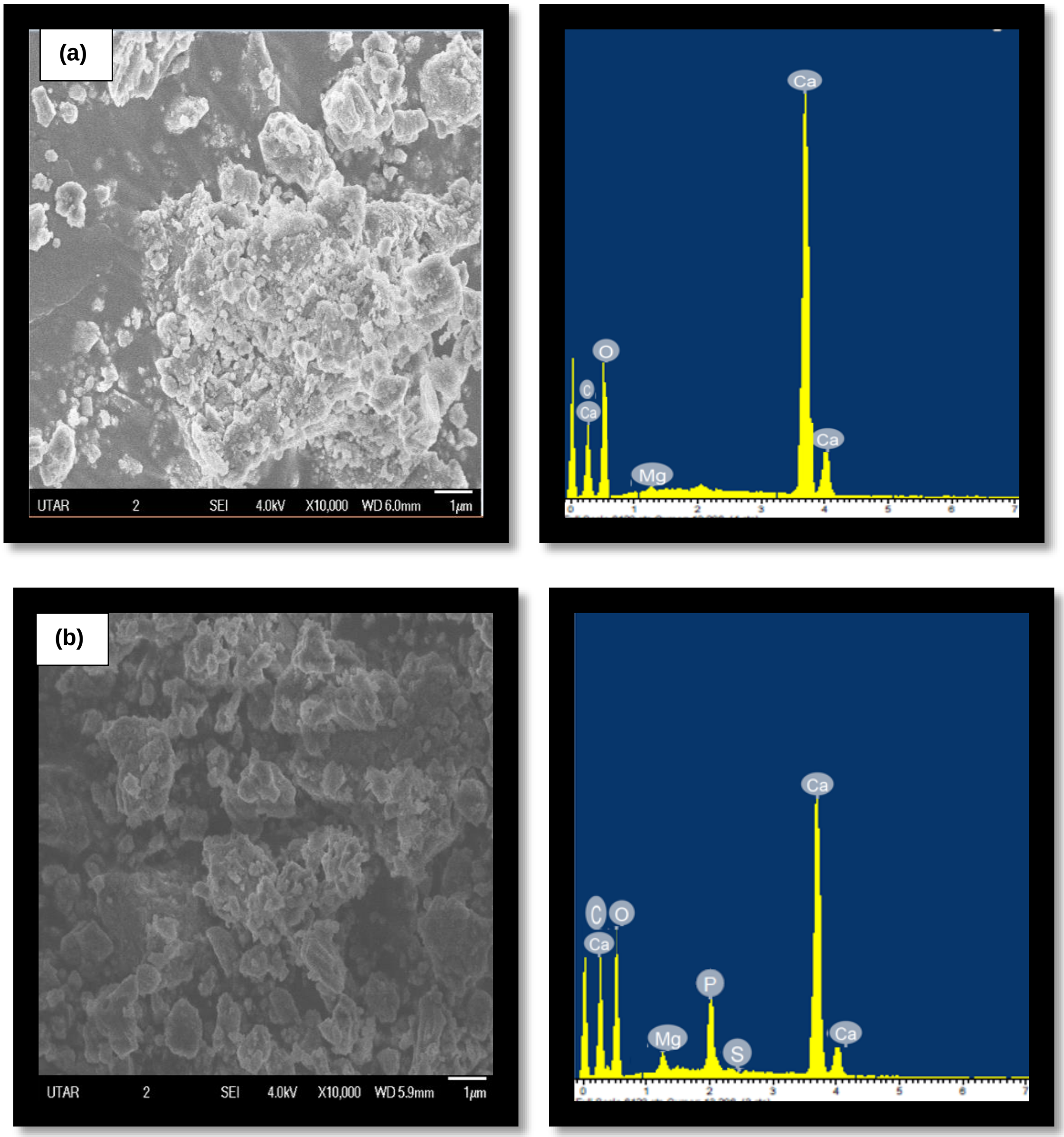


Figure 4.7: SEM and EDS Images of ESM Before SO_2 Adsorption (a) and ESM After SO_2 Adsorption (b) Under Magnification Factor 10,000X.

Table 4.4: Weight (%) of Different Chemical Composition Present in ESM Adsorbent Before and After Adsorption Process

Component	C (%)	O (%)	Mg (%)	Ca (%)	S (%)	Others (%)	Total (%)
Before	28.55	54.17	0.23	17.05	-	-	100
After	50.86	44.12	0.10	4.14	0.61	0.17	100

Others: Pb, Zn

From the EDS images, it can be seen that the intensity of the peak of Ca component had significant decrement after the SO_2 adsorption process. Besides, new peaks were discovered which attributed to the sulfur (S) and magnesium (Mg) component. The presence of the magnesium found in the EDS result after SO_2 adsorption performance as it is the minor composition that exists in the eggshell. In literature, it was reported that the eggshell compositions consist of calcium carbonate, organic matter, calcium phosphate, and magnesium carbonate (Tsai, et al., 2006). From **Figure 4.7**, the rod like structure can be seen after the SO_2 adsorption process. Al-Ghouti and Khan (2018) reported that the increase in temperature will change the circular like structure to rod like structure, which might indicate the implementation of different adsorption mechanism. Besides, the S component found in EDS indicated that the sulfur was adsorbed by the ES adsorbents. It is proven S composition appeared after adsorption process.

4.5 Economic Appraisal

In this research study, the estimated cost of the electricity consumption for eggshell-based adsorbent preparing was evaluated and tabulated in **Table 4.5**. The analysis was compared with the price of commercial calcium carbonate. According to Rahman, et al. (2017), the electricity consumption can be calculated based on the equation below:

$$Electricity\ Consumption\ (kWh) = \frac{Power\ (W) * Operation\ Hours\ per\ Day\ (hr)}{1000} \qquad (4.5)$$

Where kWh = kilowatt hour

W = Watt

Table 4.5: Electricity Consumption for Eggshell-based Adsorbent Preparation

Equipment	Purpose	Power	Time (hour)	kWh
Grinder	Sample grinding	290 W	3	0.87
Sieving machine	Sieving	750 W	0.5	0.375
Blender	Sample grinding	450 W	2	0.9
Oven	Sample drying	1800 W	8	14.4
Total electricity consumption (kWh)				16.545

Electricity Price = 16.545 kWh * 57.10 cent/ kWh

= RM 9.45

Table 4.6: Materials Required for Research Study

Materials	Purpose	Unit	Price per unit	Price
Water	Cleaning eggshell	0.02 m^3	RM 1.03 (assumed over 20 m^3)	RM 0.02
Eggshell	Raw material	1kg	-	-
Glass wool	Retain adsorbent in fix-bed reactor	1g/ time)	RM 30.12/ 100g	RM 6.02

Based on the prices listed in **Table 4.5** and **Table 4.6**, the cost to prepare the eggshell adsorbent can be easily calculated. The price of 1 kg of eggshell-based adsorbents (moisture content had been removed and ready to use for adsorption) is calculated as below:

Eggshell-based adsorbent (1kg) = Electricity Price for Eggshell Preparation + Materials Required

= RM 9.45 + RM 0.02

= RM 9.47/ kg

The price for commercial calcium carbonate per kg had been calculated as below. The cost for the oven electricity consumption to remove the moisture content had taken into account.

Commercial calcium carbonate (1kg) = Commercial Calcium Carbonate Cost per kg + Cost for oven electricity consumption

=RM 387.13/1000 kg + (43.20 kWh * RM 0.571)

=RM 25.05/ kg

Table 4.7: Electricity Consumption for the Operational SO_2 Adsorption Test (per Time)

Equipment	Purpose	Power	Time (hour)	kWh
Gas analyser	Analysed gas concentration	105	4.8 (maximum)	0.504
Mass flow meter	Controlled gas flow rate	15	4.8	0.072
Water bath	Introduced relative humidity to the gas stream	300	4.8 (maximum)	1.44
Total electricity consumption (kWh)				2.016

The **Table 4.7** above displayed the electricity consumption for the operational SO_2 adsorption test. The electricity price was calculated as below:

Electricity Price for Operational Test = 2.016 kWh * 57.10 cent/ kWh

= RM 1.15

Therefore the overall costs for the SO_2 test using eggshell-based sorbent and commercial calcium carbonate are as below:

1. *Overall cost for SO_2 adsorption test (eggshell-based sorbent)*
   = Eggshell-based adsorbent (per gram) + Operational Cost + Glass Wool (per gram)
   = RM 9.47/ 1000g + RM 1.15 + RM 0.3012
   = RM 1.46067
   ~RM 1.46 per run

2. *Overall cost for SO_2 adsorption test (commercial calcium carbonate)*
   = Commercial Calcium Carbonate (per gram) + Operational Cost + Glass Wool (per gram)
   = RM 25.05/ 1000g + RM 1.15 + RM 0.3012
   = RM 1.47625
   ~RM 1.48 per run

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Over the years, the interests of using eggshell waste as an adsorbent had been growing in different fields. In this study, the sulfur dioxide removal efficiency of ESM and ES had been studied and investigated under different parameters (particle sizes, reactor temperature, and relative humidity). Comparative study had been carried between the ESM, ES and CCC. The characteristics of the eggshell-based adsorbents were studied by SEM, EDS and FTIR analysis. The results showed that ESM had better adsorption capacity than ES due to the presence of membrane. The network of fibrous protein in ESM provides higher surface area, thus leads to better adsorption capacity. The particle size of 90 um of ESM and ES were 3.2100 mg/g and 2.7645 mg/g, respectively, whereas the particle size of 180 um of ESM and ES were 2.1950 mg/g and 1.1861 mg/g. The influence of particle size on SO_2 adsorption was explained, where the smaller particle had better SO_2 uptake compared to larger particle size. The smaller particle size tends to have larger exposed surface for the surface reaction, thus, it can provide higher contact area for the chemical reaction between the adsorbent (eggshell) and the adsorbate (sulfur dioxide gas). According to the image of SEM, it showed that the surface layer of the eggshells is irregular distributed with pores and pits, which was assumed as one of the major factors for the poor adsorption capacity. In the aspects of temperature, ESM exhibited the behaviour of low adsorption capacity at higher temperature. The sulfur dioxide lose their kinetic energy at high reactor temperature, which leads the adsorption process become exothermic. Therefore, rising of reactor temperature will permit faster chemical reaction rate of SO_2 gas. The evaluation of with and without the presence of relative humidity (RH) had been done between CCC and ESM. Both adsorbents displayed similar adsorption behaviour under both conditions. Under 40% of RH, CCC and ESM had higher adsorption capacity (18.7472 mg/g and 23.2435 mg/g, respectively) and longer saturation time (244.08 min and 290.67 min, respectively). It can be concluded that the introduction of relative humidity to the gas stream can improve the adsorption capacity, as the surface mobility ions can be enhanced. In overall, CCC tends to have better adsorption performance compared to eggshell. The major reason is CCC is 99% pure grade whilst there is some inorganic content present in the eggshell, causing lower adsorption capacity. Apart from that, the characterisation had shown the eggshell mainly consists of $CaCO_3$ component, which has a great potential for the implementation in industrial sectors.

5.2 Recommendations

From this research study, there are some improvements and several fundamental studies can be done in the future research studies. Future improvements are suggested to enhance the removal efficiency using the eggshell-based adsorbents.

1. Modification such as calcination, pyrolysis (activated) should be carried out to improve the porosity of the eggshell-based adsorbents, and the characterization of thermogravimetric analysis (TGA) should be performed.
2. The characterization analysis such as thermogravimetric (TGA) analysis and CHNOS should be performed for amount of weight change and elemental analysis, respectively.
3. XPS analysis can be performed to study the effect of binding energy of the adsorbents on SO_2 adsorption.

4. The simultaneous removal process of SO_2 and CO_2 can be studied in future due to the great adsorption performance of the eggshell-based adsorbents.
5. The parameters such as flow rate, gas pressure, dosage can be evaluated using eggshell-based adsorbent to remove sulfur dioxide gas.
6. Adsorption and desorption tests can be performed using the ESM adsorbents.
7. The amount of SO_2 had been adsorbed can be predicted and estimated using the intraparticle diffusion model regarded on Knudsen diffusion and Henry isotherm or Freundlich isotherm (Karatepe, et al., 2008).

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