FLUE GAS DESULPHURIZATION USING ADSORBENT PREPARED FROM WASTE ABUNDANT EGGSHELL

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A project report submitted in partial fulfillment of the requirements for the award of 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 that this project is based on my original work except for citations and quotations which have been duly acknowledged. I also take this opportunity to declare that it has not been previously or concurrently submitted for any other degree award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

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Flue gas desulphurization using adsorbent prepared from waste abundant eggshell

ABSTRACT

Flue gas desulphurization has been sky rocketing in recent years due to the rapid developing industry that release sulphur dioxide gas. Conventional use of commercialise calcium oxide derived from calcium carbonate has been the best adsorbent used in Flue gas desulphurization but not unsustainable. Therefore, eggshell waste has been introduced to reduce the consumption of commercial calcium oxide to prevent depletion of natural resource so that we can perform flue gas desulphurization and achieve the required standards. Using hydration method with heating mantle can greatly improve the adsorption capacity of eggshell waste by prioritizing a few parameters such as hydration temperature and hydration time. By using gas analyser to determine the gas adsorption capacity, the highest adsorption capacity of eggshell sample are achieved at 3.936 $g_{so2}/g_{eggshell}$ hydrated at 90°C and 30 hour hydration time, compare to highest adsorption capacity of commercial calcium oxide at 15.521 g_{so2}/g_{cao} hydrated at 80°C and 1 hour hydration time.

TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Egg shells

With the rapid increase in human population, there is increase in demand of food supply. Poultry products are good source of food for mankind. Egg especially, is cheap and contain high amount of nutrient such as protein, vitamins, and fat. Egg is biologically structured for the nature of reproducing organism. Egg shell is rich in calcium and it’s an abundant waste (85-95%) (Mathab et al., 2011). It provides protections and nutrient for the development of embryo. It is bio-ceramic which is rich in calcium and has combination of atomic reactivity and strength. Scientist had successfully researched the method to increase the production of eggs to supply in order to meet the demand. In Malaysia, 642,600 tonnes of egg is produced every year and since 10% of the weight of an egg is eggshell waste, a total of 70,686 tonnes of eggshell waste is generated every year. (Rohim, 2014) A medium sized egg-product processing plant can generate up to 7 tons of eggshell waste daily. This scenario increases problem in the accumulation of eggshell waste. Smaller companies overcome this issue by composting their eggshell waste to supply it to the agricultural sector. This is an effective mean of recycling until the volume of eggshell waste exceeds the demand of the agricultural field capacity. Due to the demand in cosmetic, eggshell membrane has been use to replace commercial collagen. (Mohammadi et al, 2015) Eggshell waste can also be treated by heat to sterilize it and be as mineral additive in mineral feed. (Karin Galloway 2013)

1.2 Sulphur dioxide

Sulphur dioxide (SO_2) is a group of highly reactive gas known as “oxides of Sulphur”. Sulphur dioxide released to the atmosphere resulted from the combustion of fossil fuel, volcanic activity, and smelting of sulphur-containing ores. The largest sources of SO_2 emission is fossil fuel combustion at power plants (73%)(EPA, 2014). It causes environmental and health damage. Sulphur dioxide has both acute and chronic effect on wellbeing of animal as well as human, such as respiratory irritation, heart disease, eye irritation and lung cancer (Kampa and Castanas, 2008). SO_2 is a major air pollutant which increases the mortality of living being from respiratory diseases (Lee et al., 2000).

The rapid development of our country motivated by vision 2020 had causes the pollution in Malaysia to become more severe due waste emission to water sources and atmosphere. Ample amount of awareness were raised for air pollution as the issue became more severe. The term air pollution is defined as the intrusion of foreign substance in the air that cause harm to health and human welfare, it may also trigger harmful environmental effect (Daniel, 2008). In year 2012, the highest recorded level of SO_2 which is 0.0022 ppm in the atmosphere is in the industrial area (Figure 1.1). This is mainly due to the industrial processing of material containing sulphur as well as generation of electricity from fossil fuel. Figure 1.2 shows that SO_2 contributed 6.7% to the air pollutant emitted into the atmosphere, which is the third highest pollutant. From 2011 to 2012, the emission of SO_2 increased by 10.8 % (Figure 1.3). Figure 1.4 however, shows that the industrial emission of SO_2 decreased by 35.3 % from 2011 to 2012.

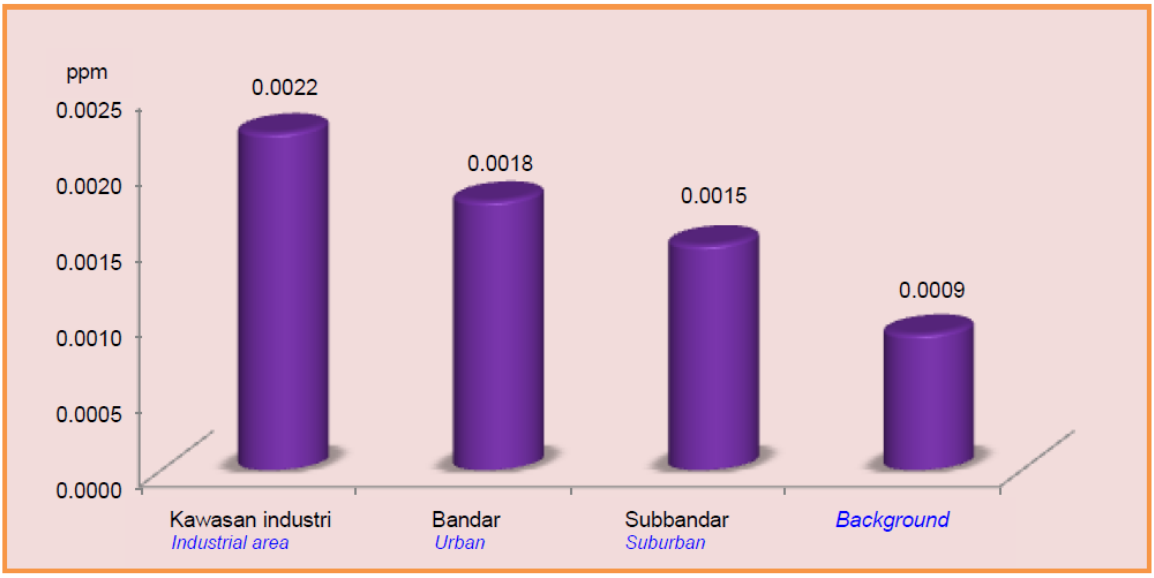


Figure 1.1 The Average annual concentration of Sulphur Dioxide by land use, Malaysia, 2012 (Department of Environment, 2013)

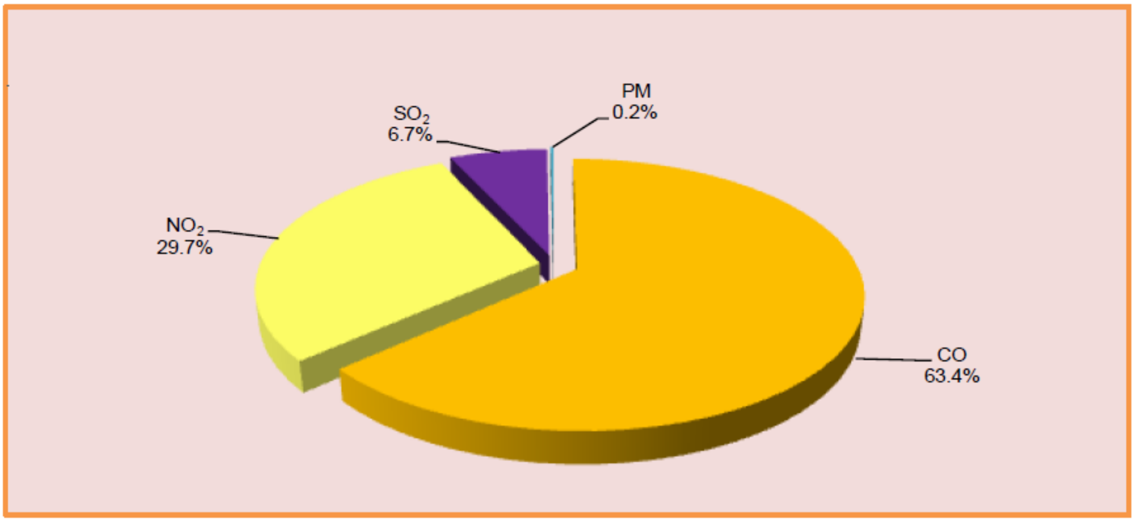


Figure 1.2 The Emission of pollutant to the atmosphere, Malaysia, 2012 (Department of Environment, 2013)

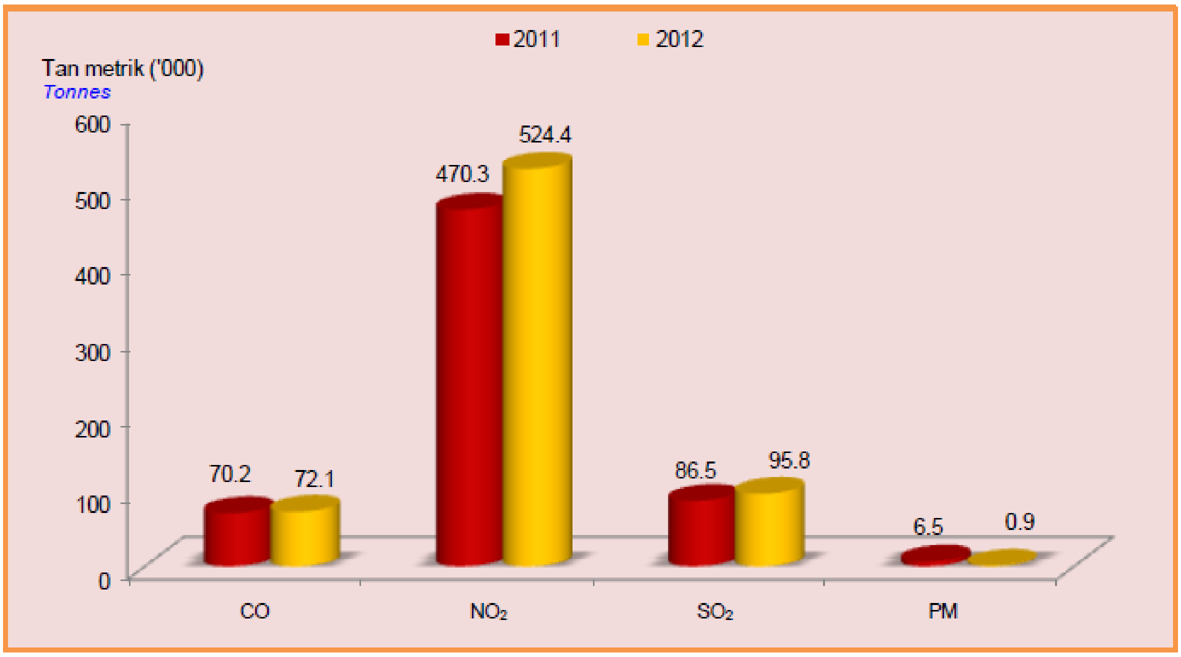


Figure 1.3 The Emission of pollutants to the atmosphere from stationary sources through power plant, Malaysia, 2011 & 2012 (Department of Environment, 2013)

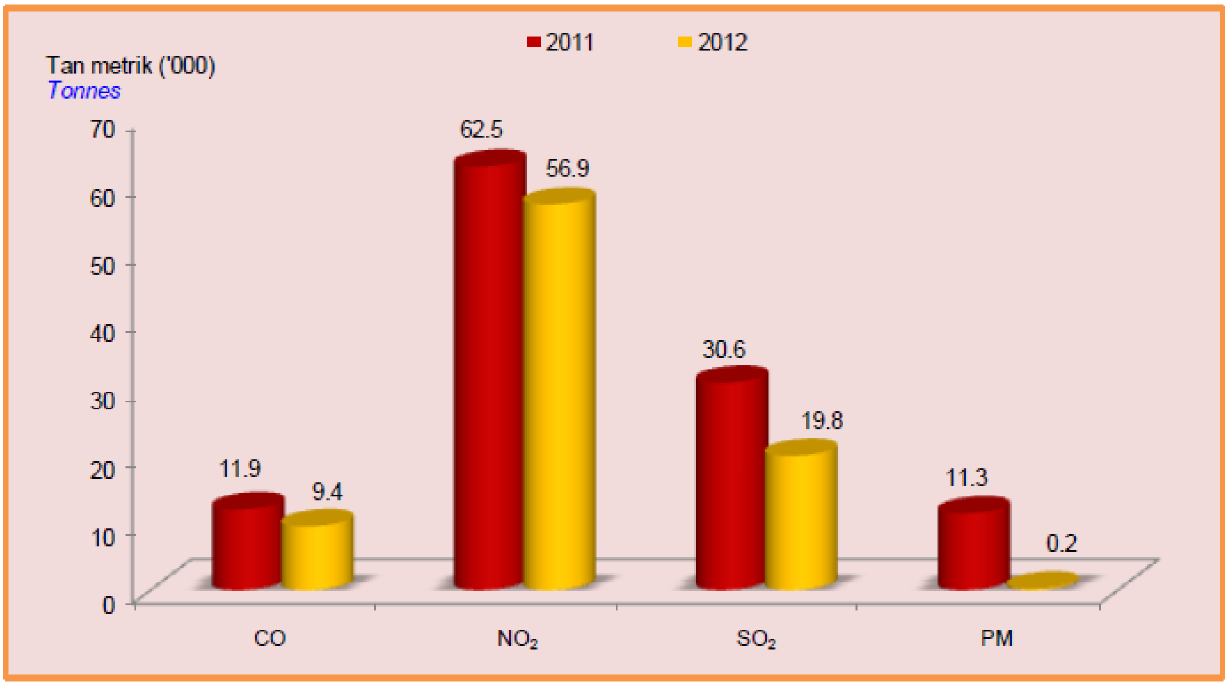
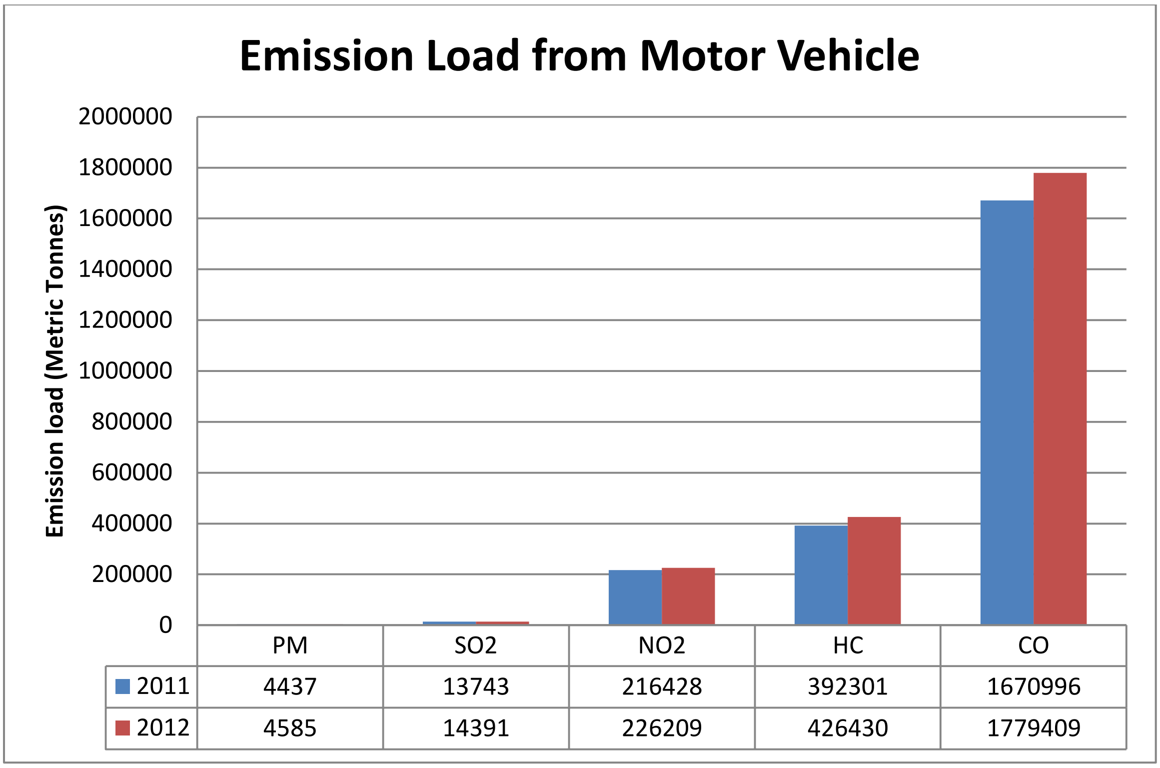


Figure 1.4 The of pollutants to the atmosphere from stationary sources through industries, Malaysia, 2011 and 2012 (Department of Environment, 2013)

Lack in efficiency of the public transportation system leads to traffic congestion and also increment of on road vehicle which could emit various pollutant into the atmosphere. With the increase in demand for transportation, the total amount of registered vehicles including passenger cars, motorcycles, good vehicles, taxis, and buses increased from 21,863,857 to 22,143,070 (Figure 1.5). Although the vehicle in use increased from 14,597,790 to 15,787,62 8(7.6 %), and contributed to about 14,391 metric tonnes of SO_2 to the atmosphere (Malaysia Environmental Report, 2012).



	PM	SO2	NO2	HC	CO
🟦 2011	4437	13743	216428	392301	1670996
🟥 2012	4585	14391	226209	426430	1779409

Figure 1.5 The emission load from motor vehicle, 2011-2012 (Malaysia Environmental Report, 2012)

1.3 Flue Gas Desulphurization

World Health Organization (WHO) set the standard for the discharge of SO_2 to maximum hourly average of 350 µg/m^3 (DOE, 2010). Hence, flue gas desulphurization technology is introduced in order for us to achieve the standard. Wet lime or wet limestone process are often used in the flue gas desulphurization process. MgO (3-8%) is added to the lime to aid in scrubbing. This process removes up to 98% of SO_2 (Liu et al, 2009). The reactions that occur during the process are:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 \cdot 0.5H_2O + 0.5H_2O$$

$$Ca(OH)_2 + SO_2 + 0.5O_2 + H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

1.4 Problem Statement

As a rapid developing country, Malaysia air pollution is high even after implementation and enforcement of law. Flue gas release from industries carries SO_2, CO and other hazardous gas. To solve the the problem, the flue gas has to be treated. Calcium oxide is often used by major industries to absrob SO_2 and form gypsum ($CaSO_4$) to treat the flue gas. Even so, the consumption of commercial calcium oxide is expensive and may be depleted. Hence in this study, egg shell and be commercial calcium carbonate will be compared with the effectiveness of flue gas treatment.

1.5 Objectives

- To optimize the preparation of egg shell and commercial calcium oxide with water hydration method.
- To evaluate the prepared adsorbent for SO_2 removal.
- Characterization of prepared adsorbent.

CHAPTER 2

LITERATURE REVIEW

2.1 Flue Gas

Flue gas are gases that release to the environment via channel or pipe for transporting exhaust gases from industry which consist of combustion in their process such as furnace, coal-power plant, and etc. Through the change of energy from chemical to heat energy, the combustion of coal, oil or petroleum through oxidation process is known as combustion. Fossil fuel generates flue gas during combustion. The composition of the gas depends on the material use in the combustion process. Common residual substances found in the flue gas from the combustion plants are particulate matter, sulphur oxides, nitrogen oxides and carbon monoxide. The presence of HCI, HF, hydrocarbons and heavy metals in the flue gas could be also detected in the case of waste material incineration (Lawrence, Norman and Hung, 2005).

The discharge of Sulphur Oxides (SOx) to the environment can be originated from natural and anthropogenic sources. Power plant that uses fossil fuel are the main anthropogenic emission sources which contributed 69.7%, about 13.6% of total global SOx emission (Liu et al, 2010). Other than that, according to DOE, in 1996, Malaysia, the percentage of the air emission load by type of discharge were: motor vehicles at 82%, power station at 9%, industrial fuel burning at 5%, industrial production processes at 3 %, domestic and commercial furnaces at 0.2 %, and open burning at waste disposal sites at 0.8%. (DOE, 1996)

2.1.1 Composition and effect of flue gas

The flue gas composition is highly dependent on the type of combustion material as well as the condition. Flue gas contains air pollutants that require special treatment to meet the standard before releasing it into the atmosphere. Fossil fuel power plants release a large amount of SO_2, NOx, mercury, particulates, and other trace elements. Study shows that an average coal-fired plant generates 3.7 million tons of CO_2, 10 kilotons of SO_2, 10.2 kilotons of Nitrogen Oxides (NOx) which are the top 3 pollutant in the atmosphere (Liu et al,2010).

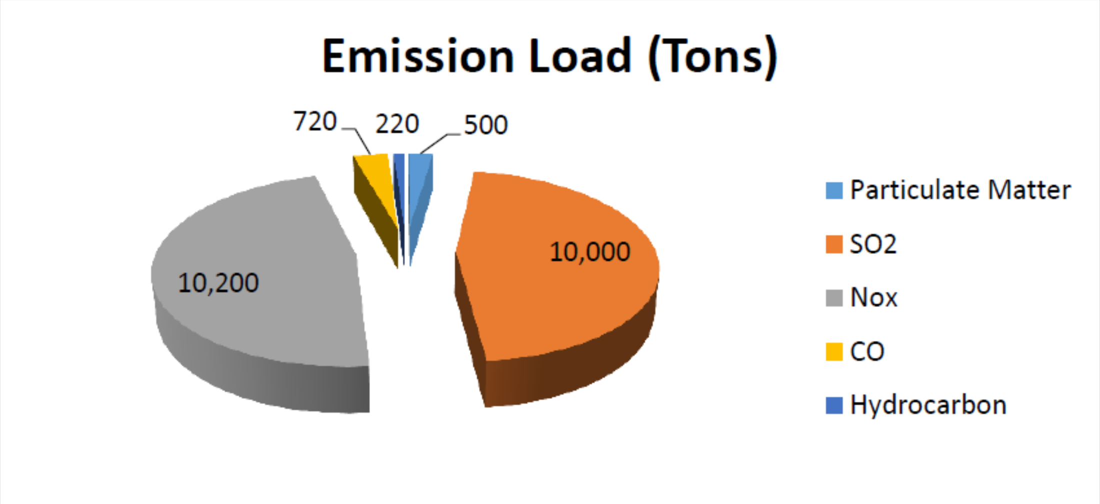


Figure 2.1 Composition and Emission Load from Flue Gas (Liu et al,2010)

Flue gas creates air pollution which causes adverse effect to human health. This is due to the composition of flue gas which contains gas released from fossil fuel plant that is hazardous such as nitrogen oxides, sulphur oxides and etc. Table 2.1 provides a brief explanation of air pollutants from figure 2.1 and the health effect.

Table 2.1 Air Pollutants and Associated Health Effects (Daniel, 2008)

Pollutant	Effect on Health
CO	• Reduce the ability of blood to transport oxygen • Task which requires vigilance will shows impairment of performance • Exacerbate of cardiovascular disease
NO_2	• Causes lung to be more prone to respiratory pathogens
SO_2/ Particulate matter	• Increased extensiveness of chronic respiratory disease • Increased risk of acute respiratory disease
Hydrocarbon	• Causes eye and respiratory irritation

2.2 Sulphur Dioxide

Sulphur dioxide is a compound of on sulphur atom associated with two oxygen atom. It is commonly released from sulphur-containing ore smelting industry, fossil fuel combustion chamber, and vehicles. It is also naturally emitted from volcano as volcanic gases.

Sulphur dioxide is uncolored, irritant and soluble in water. It can be tasted by human taste bud at concentration of 0.35-1.05 ppm and by sense of smell of a pungent irritating odor at 3.5 ppm (Lawrence, Norman & Yung, 2005). More of the physical characteristic of sulphur dioxide can be seen from table 2.2.

Table 2.2 Physical properties of sulphur dioxide (Lawrence, Norman and Hung, 2005)

Parameter	Characteristic
Color	Uncolored
Odor	Pungent and suffocating
Taste	Sour
Vapour density	32 (2.2 times heavier than air)
Solubility in water	Fairly soluble
Boiling point	-10°C
Freezing point	-76°C
Physiological nature	Poisonous

Sulphur dioxides in the air are able to combine with oxygen to form SO_3, which can further react with water to produce H_2SO_4. Sulphuric acid can be formed from reaction of water with dissociated from sulfite and bisulfite ions. Sulphuric acid are harmful to living being as well as the environment. Sulphur dioxide is a reducing agents, it reacts with water molecules to produce hydrogen ions which assist in the reducing action ($SO_2 + H_2O \rightarrow H_2SO_4 + 2H$). Sulphur dioxide reducing property also shows addition reactions in the presence of oxygen ($2SO_2 + O_2 \rightarrow 2SO_3$). On the other hand, sulphur dioxide also shows oxidizing property when come in contact with burning potassium magnesium metal ($2Mg + SO_2 \rightarrow 2MgO + MgS$) (Lawrence, Norman and Hung, 2005).

2.3 Flue Gas Desulphurization (FGD)

The purpose of FGD is to get rid of sulphur compounds from the flue gas. It is mostly used in oil refining, coal and pyritic sulphur in the coal cleaning (Lawrence, Norman and Hung, 2005). There are several categories of innovative creation for FGD, which are spray dry scrubber, wet scrubbers, absorbent injection processes, dry scrubber and etc,. The most common method of FGD is wet desulphurization method utilising limestone as absorbent which provide high removal efficiency (99%) of the sulphur dioxide (Kallinikos et al, 2010).

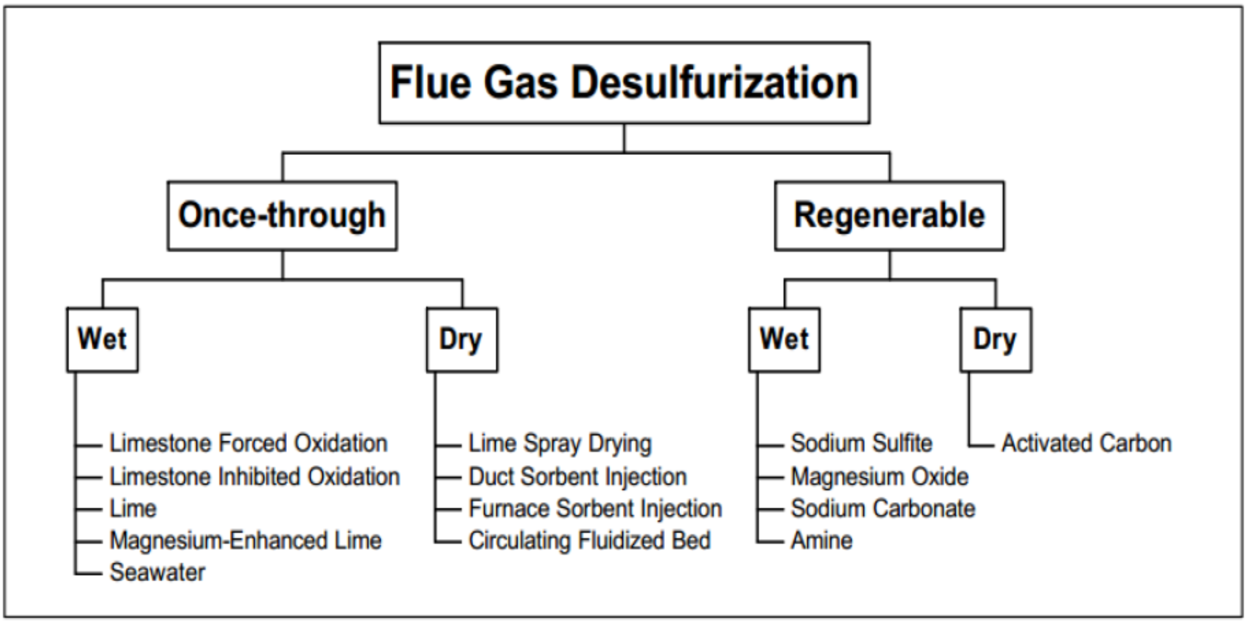


Figure 2.2 Various types of FGD (Kallinikos et al, 2010)

2.3.1 Conventional Coal Cleaning

In conventional coal cleaning process, coal is crushed into size smaller than 50mm in diameter and filtered into coarse-medium, and fine particle size fraction. Minerals with organic rich coal with higher density can be separated from the course-intermediate particles coal by dense-medium baths, cyclone systems, and jigs. The sulphur removal from this physical cleaning process is from 40-90% of total sulphur content in coal. Table 2.3 list some of the advantages and disadvantages of conventional coal cleaning in FGD (Lawrence, Norman & Hung, 2005).

Table 2.3 Pros and cons of physical coal cleaning (Lawrence, Norman and Hung, 2005)

Advantages	Disadvantages

10%-40% lower SO_2	Coal grinding is energy intensive
Higher pulverizer and boiler availability	Water-based coal cleaning methods add moisture to the coal, which reduces boiler and power plant efficiency
Lower maintenance cost	2- 15% of energy loss occurred during cleaning
Less boiler slagging and fouling	
Lower dust loading for ESP/Bag filter	
Lower transportation costs	

2.3.2 Fluidized Bed Combustion (FBC)

Sulphur oxides which are released from stacks are controlled by combining the SO_2 adsorbent and coal initially at the point of combustion. This is done by injecting limestone to coal prior entering the boiler. Fluidized bed combustor provides sufficient contact time for fuel and limestone to react. Figure 2.3 shows the mechanism of the FBC consisting of air inlet into the bed of adsorbent filled with coal and limestone to treat the flue gas and lastly discharged to the atmosphere through the stack.

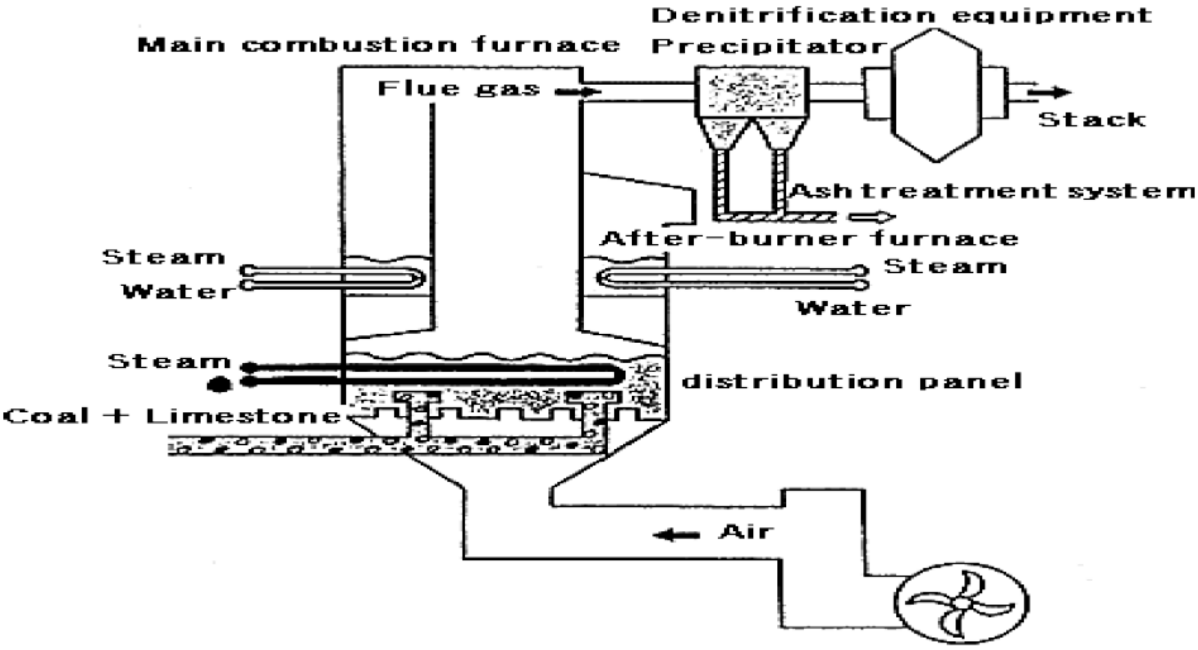


Figure 2.3 Fluidized Bed Combustor

In FBC, a box containing crushed limestone bedding is supported by grid. Air is then pressured through the grid that is in condition to create turbulence and causes the limestone bedding to behave like suspended solid and perform fluid like motion. Later, the firebox is ignited followed by coal pulverizing and gas injections. Sulphur which are oxidized during combustion reacts with limestone to form gypsum. The FBC method has the sulphur dioxide removal efficiency of more than 90% during combustion (Lawrence, Norman & Yung, 2005).

2.3.3 Forced Oxidation Limestone Wet Scrubber

This is one of the most widely used way to handle the removal of SO_2 from flue gas. Figure 2.4 below shows the processes on the forced oxidation limestone wet scrubber. Firstly, the flue gas undergoes solid fly ash particles removal. It is then passes to the next scrubber where it passes countercurrent to scrubbing slurry that contains limestone particle and water. Some design relies on high open area in the tower. In the tower, the SO_2 dissolved in the slurry reacts with limestone producing

Carbon Dioxide, which enter the gas stream, and a solid $CaSO_3$. Then, the $CaSO_3$ is oxidized to $CaSO_4$.

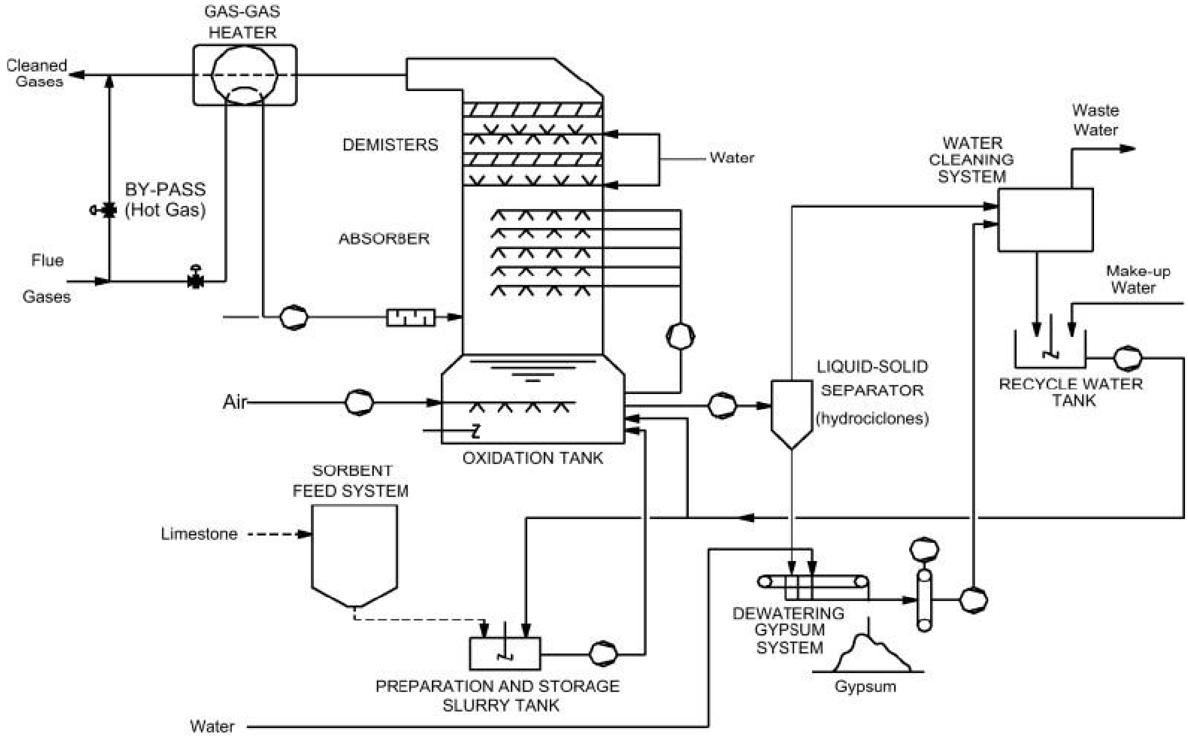


Figure 2.4 Flow Diagram for forced-oxidation limestone wet scrubbing

2.3.4 Spray Dryer

Spray dryer are commonly utilized in the process industries. In the spray dryer mechanism, fluid which contains dissolved or suspended solids is scattered as droplet into a hot gas stream. The dispersed droplet is heated above the boiling point of water such that the droplet evaporates quickly. The spray dryer is widely used when the product is easily influence by temperature change. Every step of drying and powder cooling is done quickly as it leaves the dryer. For the SOx treatment, flue gas enters the spray dryer chamber from the side and through an outlet pipe that is dipped into a dryer vessel. The reagent slurry is then disperse leaving about 30% solid weight. The remaining dry matter are small minute enough to be carried along with the gas stream. The primary reaction that occurs in the spray dryer is shown as:

Ca2+ (aq) + SO2- (aq) + 0.5 H2O □ CaSO3·0.5 H2O (s)

Ca 2+ (aq) + SO4

2- (aq) + 2H2O □ CaSO4· 2H2O (s)

CaSO3 + 0.5 O2 □CaSO4(s)

Spray dryer is also called wet-dry system due to its process combining both wet lime scrubber technology and dry sorbent injection method. The SO_2 dissolved in the water reacts with $Ca(OH)_2$. As the water evaporates, the fine particles are filtered in the filter bag. Figure 2.5 shows the flow diagram as to how the spray dryer process works to remove SO_2 from flue gas.

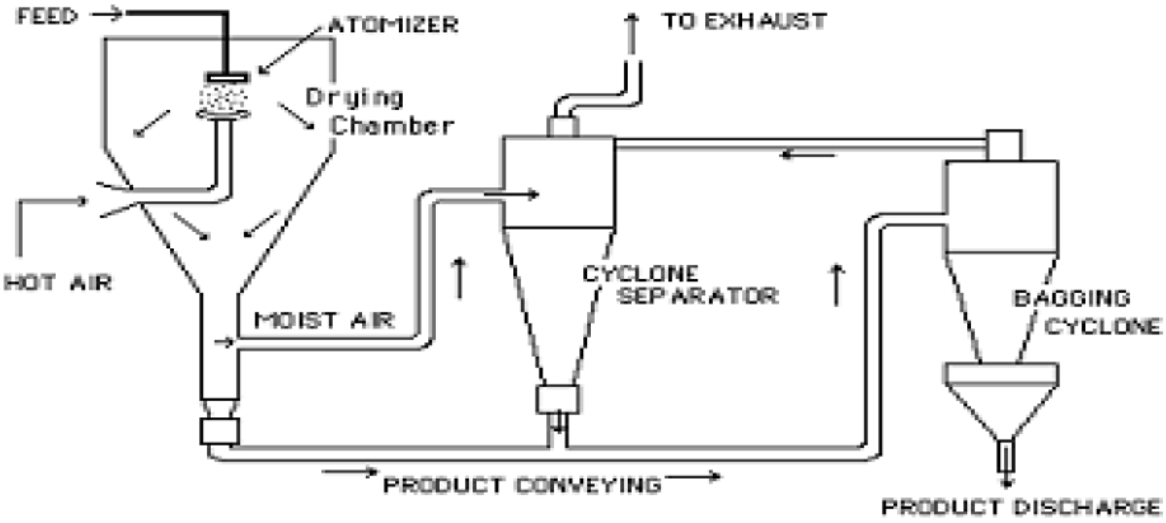


Figure 2.5 Flow diagram for spray dryer process for removal of SO_2 from flue gas

2.3.5 Adsorption

Adsorption is the adherence of material to the surface of porous solids. This system removes low concentration gases and vapours from exhaust stream. With wise selection of adsorbent and contact time between the adsorbent and flue gas, high removal efficiencies are achievable. Gas adsorption can be applied in industry for odor control, volatile compound recovery, and drying of process gas stream (Louis, 2008). Adsorption can be described in two categories which are physical or chemical. The fundamental difference of the two is the way the adsorbate bound to the adsorbent.

For physical adsorption, the molecule is bounded to the adsorbent surface by a weak intermolecular force. The chemical properties of the molecule and the adsorbent remain unchanged in the process, hence it is reversible. The forces acting in the cohesion between the molecule and adsorbent is electrostatic in nature. It is known as Van der Waals force. Van der Waals is an electrostatic forces that presence in all matter. The strength of the force depends on the polarity between two molecules (David, 2002). Physical adsorption can be caused by three different factors: Orientation effect, a dispersion effect, or induction effect. Polar molecules attract to each other due to the orientation effect. The orientation effect refers to dipoles-dipoles interaction (Louis, 2008).

A stronger bond will be created between the molecule and adsorbent in chemical adsorption due to exchange of electron in chemical bond. Since it involve in altering the chemical structure of the molecule and adsorbent, the process cannot be easily reversed. The adsorbent used can be in the form of pure subtances or chemical deposited on an inert carrier surface. One example is that we can use activated carbon filled with sulphur to remove mercury vapour (David, 2002).

2.3.5.1 Adsorbent Material

Some common adsorbent materials used in different industry for gas removal application are activated carbon, silica gel, zeolites, and activated alumina. Adsorbent are distinct by their chemical properties, surface contact area, pore distribution, and particle size. Table 2.4 displays the different adsorbent used to treat SO_2 gas.

Table 2.4 Adsorbent used to treat SO_2 in flue gas

Adsorbent	Reference
Commercial activated carbon	Asasian et al, 2013
Pumice	Ozturk & Yildirim, 2006
Rice husk ash	Dahlan et al, 2009
CaO with fly ash	Lee et al, 2008
CaO with oil palm ash	Lee et al, 2008
CaO with single oxide	Mathieu et al, 2013
Activated coke	Li et al, 2008
South Africa limestone	Ogenga et al, 2010
Coal fly ash based carbon	Rubio & Izquierdo, 2010

2.3.5.2 Water Hydration Method to prepare Adsorbent

Water hydration method is the reaction between calcium dioxide and pure water that is heated and quick. It’s difficult to control the hydration process in order to acquire calcium hydroxide sorbent with optimum adsorption (Shin et al, 2008). It was tested that the presence of water in gas would decrease the adsorption capacity; however, low ratio of water may have opposite effect. Then, if hydrates could form in the pore of porous adsorbent, the gas adsorption capacity will increase dramatically. (Zhang et al, 2013)

2.4 Eggshell

Chicken eggshells consist of two main components, the eggshell membrane matrix that is made out of spherical masses and protein fibres, and the spongy matrix that is made out of interstitial calcite or calcium carbonate crystals (Li-Chan et al, 1995). Eggshell are made out of magnesium carbonate (1%), organic matter (4%), calcium phosphate (1%), and calcium carbonate (94%) (Stadelman, 2000). Eggshell waste is often ended up in the landfill for disposal.

2.4.1 Usage of eggshell

High calcium, phosphorus, and magnesium content of the waste eggshell are reused as fertilizer, soil conditioner or additive for animal feed. The abundance amount of eggshell waste and intrinsic pore structure made it practical to grind eggshell waste into fine powder which may replace multiple materials such as limestone as adsorbent. Table 2.5 below show the different uses of eggshell from different journals.

Table 2.5 Usage of eggshell from literature

Usage of eggshell	Reference
Adsorbent for the removal of dyes from aqueous solution	Tsai et al, 2008
Biocomposite eggshell adsorbent to remove reactive red dye	Elkady et al, 2011
CO^2 sorbent with the characterization of calcium oxide derived from waste eggshell	Wiltoon, 2011
Adsorption of phosphate from aqueous solution using calcined waste eggshell	Ennil & Kivanc, 2011
Removal of heavy metal with calcined eggshell powder	Oliveira et al, 2013
Calcium oxide derived from eggshell used as catalyst in biodiesel production	Oliveira et al, 2013

CHAPTER 3

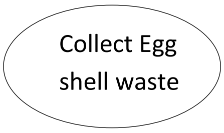
RESEARCH METHODOLOGY

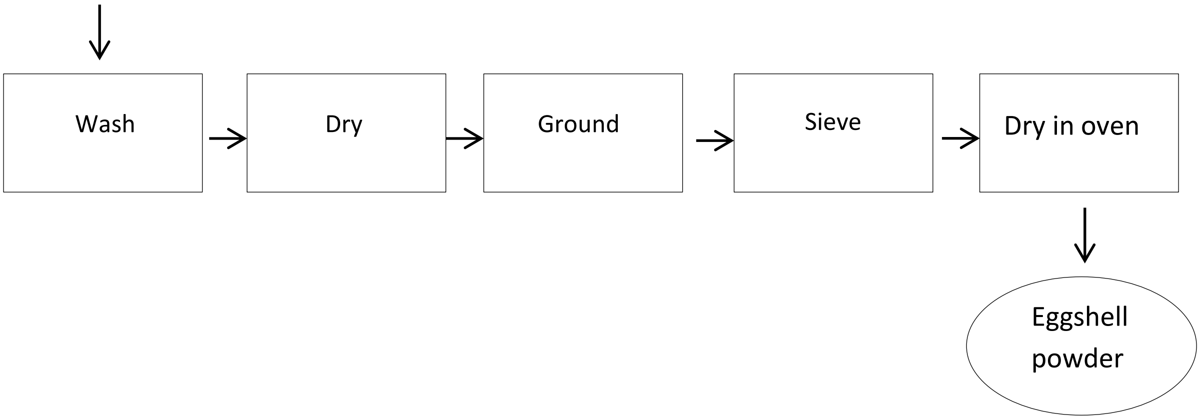
3.1 Raw materials

The materials that will be used in this project are commercial calcium carbonate, eggshell waste, and sulphur dioxide gas. The egg shell waste was collected frequently around the canteens in UTAR, cake shops and etc. The sulphur dioxide gas is purchased from LINDE MALAYSIA Sdn.Bhd. in a form of compressed gas of 2000 ppm.

3.2 Preparation of eggshell powder

The collected eggshell will be wash with detergent to remove egg residue and egg membrane. It is then dried and ground into powder. The eggshell powder will be sieved to obtain an average particle size of 63μm. Lastly it is further dried in the vacuum oven at 105°C until a constant weight is obtained.





3.3 Preparation of Adsorbent

Eggshell powder which is rich in $CaCO_3$ were calcined for 2 hours at 800°C to obtain calcium oxide (Zainudin et al, 2011). The calcined eggshell powder will be treated with water hydration method. Four grams of the calcined eggshell powder was placed into 400ml of water. Then the slurry was mixed and heated to a selected hydration temperature for a designated time as per the parameter designed. The resulting slurry will be filtered and dried at 105°C for 24 hours. The dried adsorbent will be pelletized, crushed and sieved.

Eggshells and commercial calcium oxide were prepared with the following parameter in the using the water hydration method. Table 3.1 shows the experimental design parameter.

Table 3.1 Design parameter of eggshell and commercial calcium oxide

Eggshell/Commercial CaO Code	**Hydration Time, hr**	**Temperature, °C**
A1	1	80
A2	1	90
A3	1	100
B1	3	80
B2	3	90
B3	3	100
C1	5	80
C2	5	90
C3	5	100
D1	10	80
D2	10	90
D3	10	100
E1	30	80
E2	30	90
E3	30	100

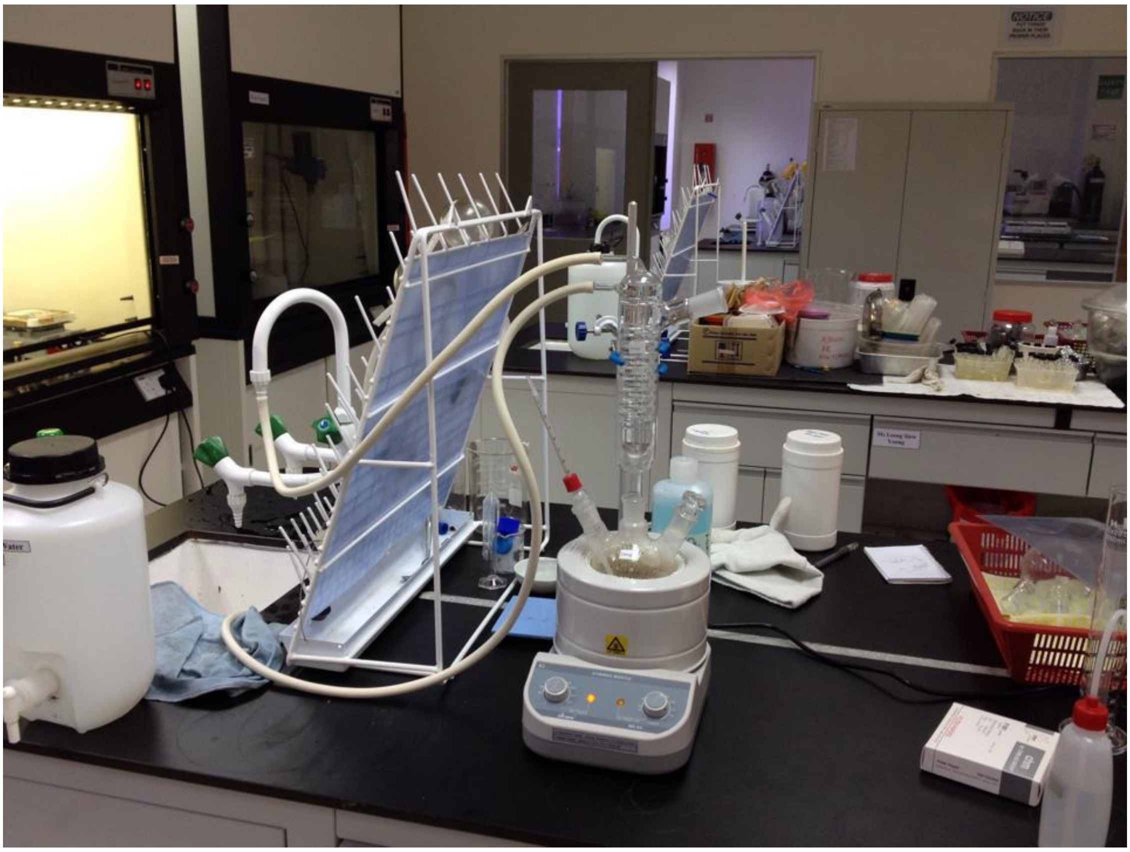


Figure 3.1 The apparatus setup for the preparation of adsorbent

3.4 Sulphur dioxide removal

Sulphur Dioxide gas of 2000 ppm is transferred across the pipe at 100 ml/min into a flask containing water heated to 80°C to increase the humidity of the gas to 20%. The gas leave the flask enters the oven that is also heated to 80°C. In the oven, there’s a tube which contains the adsorbent of 1gram of eggshell or 0.1gram of CaO. The Sulphur Dioxide gas passes through the adsorbent and lastly into the MRU Air Gas Analyzer manufactured by Varioplus Industry. The results obtained from the Gas Analyzer provide a graph of concentration of SO_2 against time.

Figure 3.2 The apparatus setup for the sulphur dioxide test

3.5 Characterization

The following is the method of characterization to identify the physical and chemical properties of eggshell and commercial calcium carbonate.

3.5.1 Fourier Transform Infrared Spectroscopy (FTIR) analysis

Fourier Transform Infrared Spectroscopy method uses the emission of infrared electromagnetic wave to pass through a specimen. The infrared will be partially dispersed, transmitted and partially absorbed by the tested object. The resulting spectrum indicates the molecular adsorption and transmission. This detector would then create a resulting spectrum of the transmission and emission, like a molecular fingerprint of the sample. FTIR is use for the examination of functional groups on the surface of activated clays or carbon material (Tsai et al., 2001, 2002). FTIR is a technique used to obtain infrared spectrum of emission, photoconductivity, or adsorption of a solid, liquid or gas. It collects high spectral resolution data over a certain spectral range.

3.6 Calculating adsorption capacity

The formulas used for calculating adsorption capacity are as follow (Konduru, 2007):

$$S_{Cap} = M_A / M_{Media}$$

Where,

S_{Cap} = Adsorption capacity of the absorbent, $g_{so2}/g_{adsorbent}$

M_A = Total mass of adsorbate adsorbed, g_{so2}

M_{Media} = Mass of the adsorbent media, $g_{adsorbent}$

In order to calculate M_A, use the formula:

$$M_A = (A_t M_{tot}) / A_{tot}$$

Where,

A_t = area above the curve at time t, ppm_v min

M_{tot} = The mass passing through the scrubber at time t_{90}, minute

A_{tot} = Total area at time t, ppm_v min

In order to calculate M_{tot}, use the formula:

$$M_{tot} = Q \times t_{90} \times \rho_{so2}$$

Where,

Q = volumetric flow rate of SO_2, L/min

T_{90} = time when the concentration at 90%, minutes

ρ_{so2} = density of SO_2 during adsorption, g/L

In order to calculate A_{tot}, use the formula:

$$A_{tot} = C_{inf} \times t$$

Where,

C_{inf} = influent concentration of SO_2 ppmv

t = time, minutes

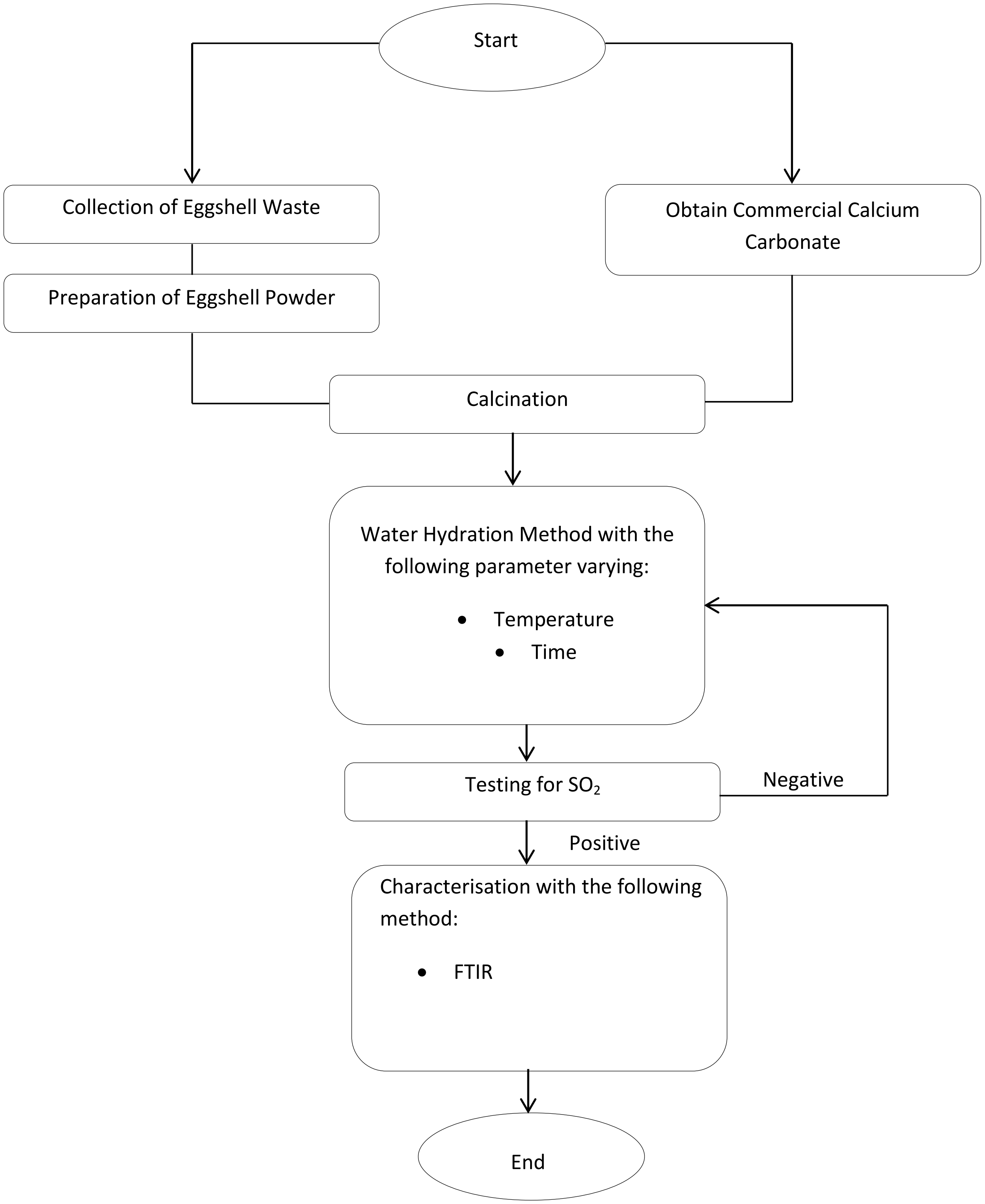
In order to calculate A_t, use the formula:

$$A_t = \int_0^t (C_{inf} - C)\, dt$$

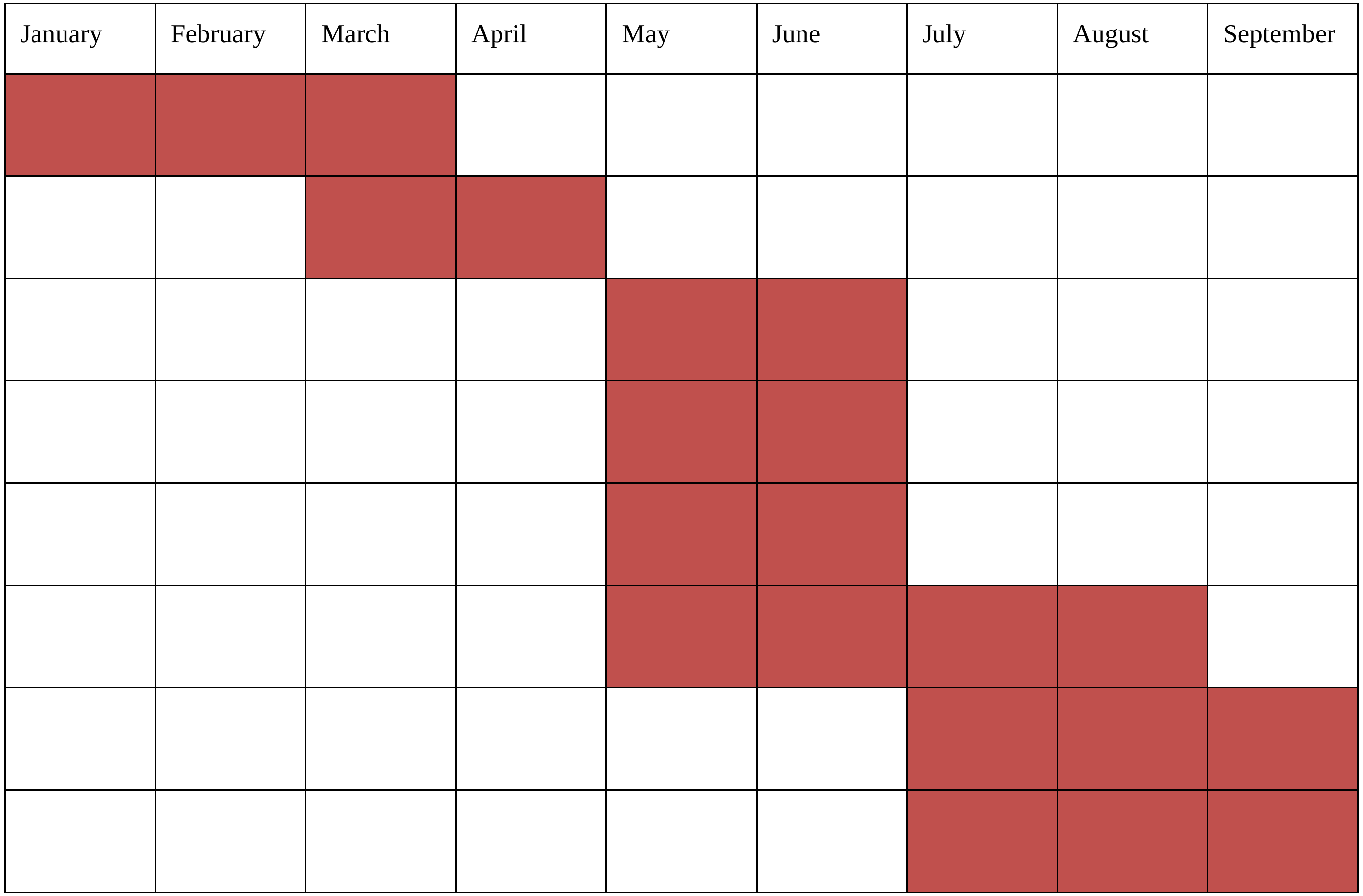
Where,

C = concentration of SO_2 at time t, ppmv

3.7 Overall experiment



3.8 Gantt chart



January	February	March	April	May	June	July	August	September
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	Literature Review	Material Collection	Adsorbent Preparation	SO_2 Testing	Data Collection & Analysis	Characterisation	Result and Discussion	Thesis Writing

CHAPTER 4

RESULT AND DISCUSSION

4.1 Sulphur dioxide removal efficiency

Figure 4.1 to Figure 4.10 shows the graph of concentration of SO_2 in ppm against time in minutes. Figure 4.1 to Figure 4.5 represent are showing the result from eggshell samples of 1 hour, 3 hours, 5 hours, 10 hours, and 30 hours hydration time. Their hydration temperature is 80°C, 90°C and 100°C. Figure 4.6 to 4.10 are showing the result obtained from commercial calcium oxide samples of 1 hour, 3 hours, 5 hours, 10 hours, and 30 hours hydration time. Their hydration temperature is 80°C, 90°C, and 100°C. These graphs enable us to calculate the adsorption capacity using equation.

Figure 4.1 shows that the eggshell with 1 hour hydration time and 80°C start up very slow but rocketed to saturation point, which indicates that it has a good adsorption capacity before breakthrough. While the other two graph of 90°C and 100°C proceeded smoothly all the way to saturation point. The 100°C graph took the longest time to reach saturation, but has lower adsorption capacity because the time it takes to reach 90% concentration is shorter than 80°C.

For figure 4.2, it shows that the eggshell of 100°C graph of 3 hour hydration time slowly increase in concentration and took the longest to complete. But for 80°C and 90°C, the graph shows rapid increase in concentration, hence indicate that it is not a very good adsorbent.

Moreover, figure 4.3 shows the eggshell with 5 hour hydration time with all the graph steadily arrived saturation with 80°C took the longest time and 90°C use the shortest time. While 90°C graph took shorter time to reach saturation than 80°C graph, the 90°C adsorption capacity is higher because it took longer for the concentration to hit 90% compare to 80°C.

Figure 4.4 show the result of eggshell of 10 hour hydration time. The 100°C graph shows that it took the longest time to reach 90% concentration as well as the longest time to hit saturation, hence it demonstrate the best adsorption capacity compare to 80°C and 90°C.

Figure 4.5 show the graph of 30 hour hydration time of eggshell, with 90°C having the highest adsorption capacity among eggshell sample; this is because it take the longest time for it to hit 90% concentration, as well as the longest time for it to hit saturation. It performs far better off than 80°C and 100°C which hit saturation at only 20 minute.

On the other hand, figure 4.6 shows the result of CaO with 1 hour hydration time, the graph of CaO took almost double the time for it to hit saturation compare to eggshell, although it uses 10 times less adsorbent compare to eggshell. This shows that CaO generally have better adsorption capacity. The 80°C, 90°C and 100°C all took about the same time to reach saturation, but 90°C and 100°C graph reach the 90% concentration faster, hence 80°C demonstrate that it has higher adsorption capacity.

Figure 4.7 shows the result of CaO with 3 hour hydration time, the highest adsorption capacity is 100°C, and the lowest is 80°C. The 100°C graph took longer to complete, as well as took longer time for it to hit 90% concentration.

Figure 4.8 shows the result of CaO with 5 hour hydration time, the highest adsorption capacity is 100°C. This is because the graph of 100°C took the longest for it to hit 90% concentration.

Furthermore, figure 4.9 shows 10 hour hydration time for CaO. Although they took about the same time to hit saturation. But the best adsorption capacity is 100°C, because it took longer to reach 90% concentration and adsorbed more SO_2 along the way.

Lastly, figure 4.10 shows 30 hour hydration time of CaO. The 90°C graph took the longest to reach saturation and also took the longest to hit 90% concentration, therefore, it has higher adsorption capacity compare to 80°C and 100°C.

All graph starts with zero, and slowly breakthrough of adsorption column occurs as the removal efficiency of the adsorbent deteriorate and SO_2. The concentration of SO_2 that enter the gas analyzer increase rapidly until it reaches the saturation point (Khalil, 2011). Graphs that show curve with the longest period take before breakthrough and hit 90% concentration will indicate that the sample have higher adsorption capacity. Also, graph that take longer to reach saturation point will have better adsorption capacity because of the total amount of SO_2 adsorbed will be higher. Lastly, if the area above the graph is bigger, it will indicate that the adsorbent have higher adsorption capacity. (Konduru, 2007)

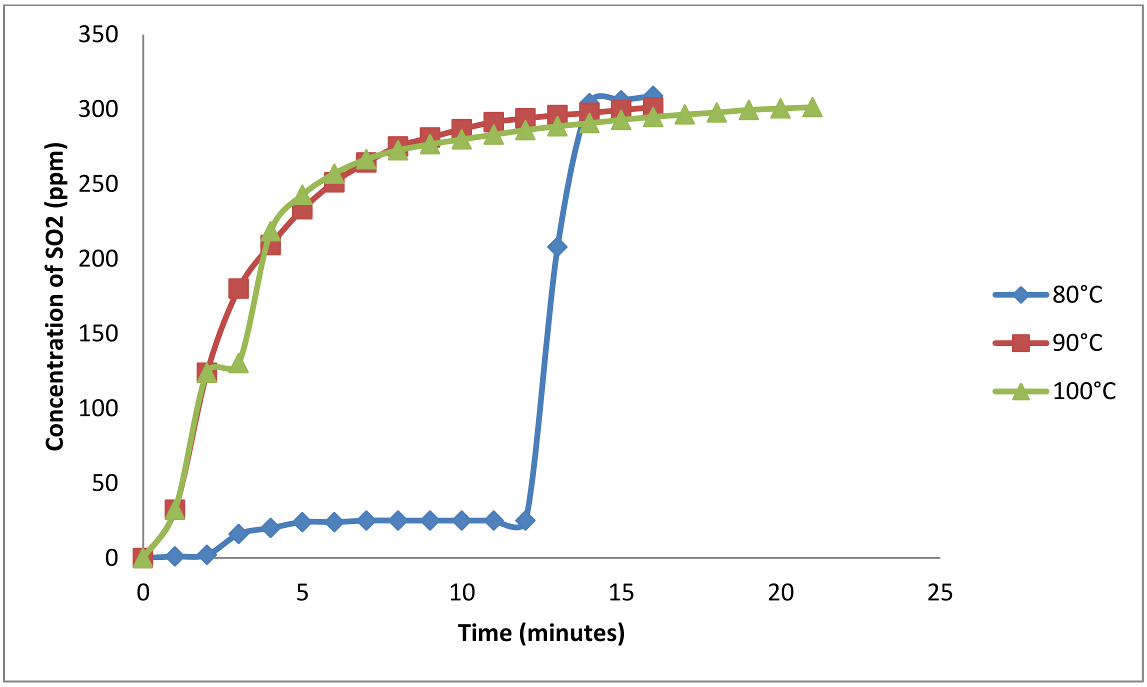

Figure 4.1 The result of eggshell with 1 hour hydration time

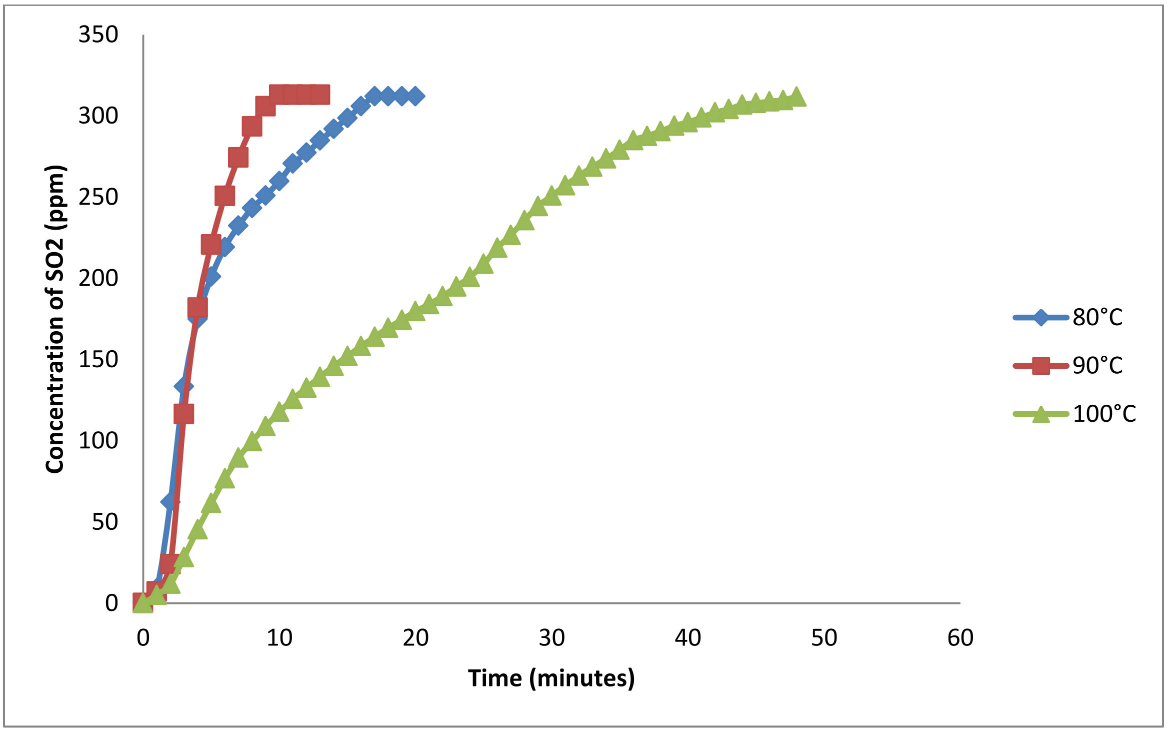

Figure 4.2 The result of eggshell with 3 hour hydration time

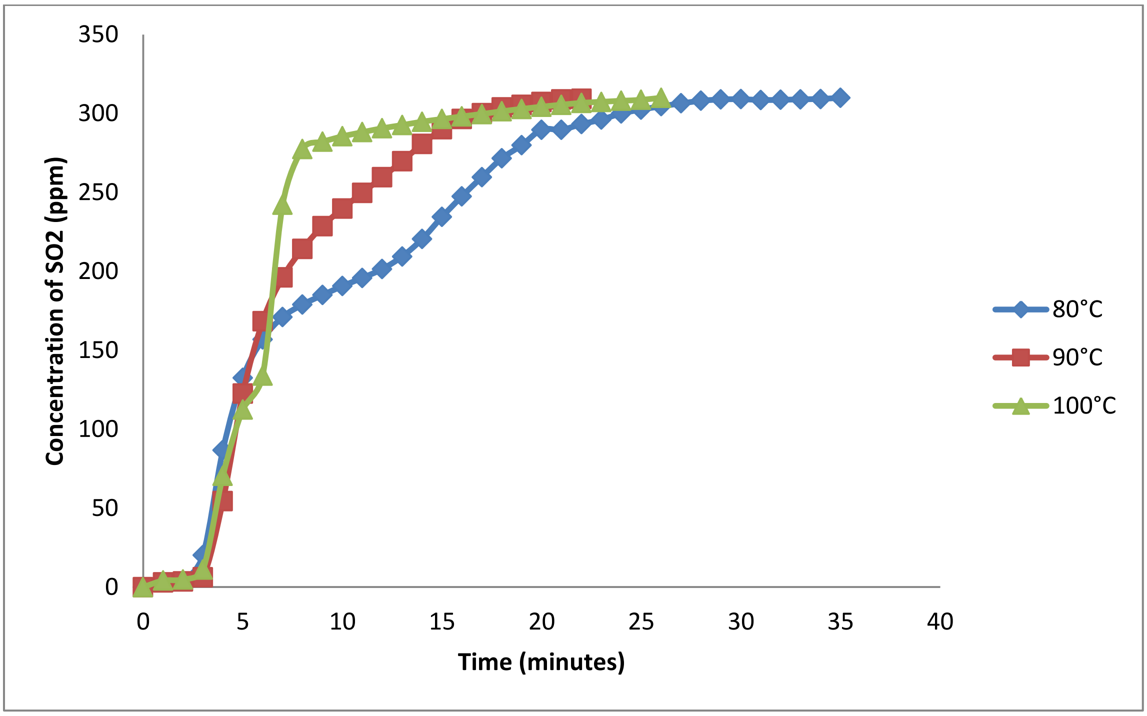

Figure 4.3 The result of eggshell with 5 hour hydration time

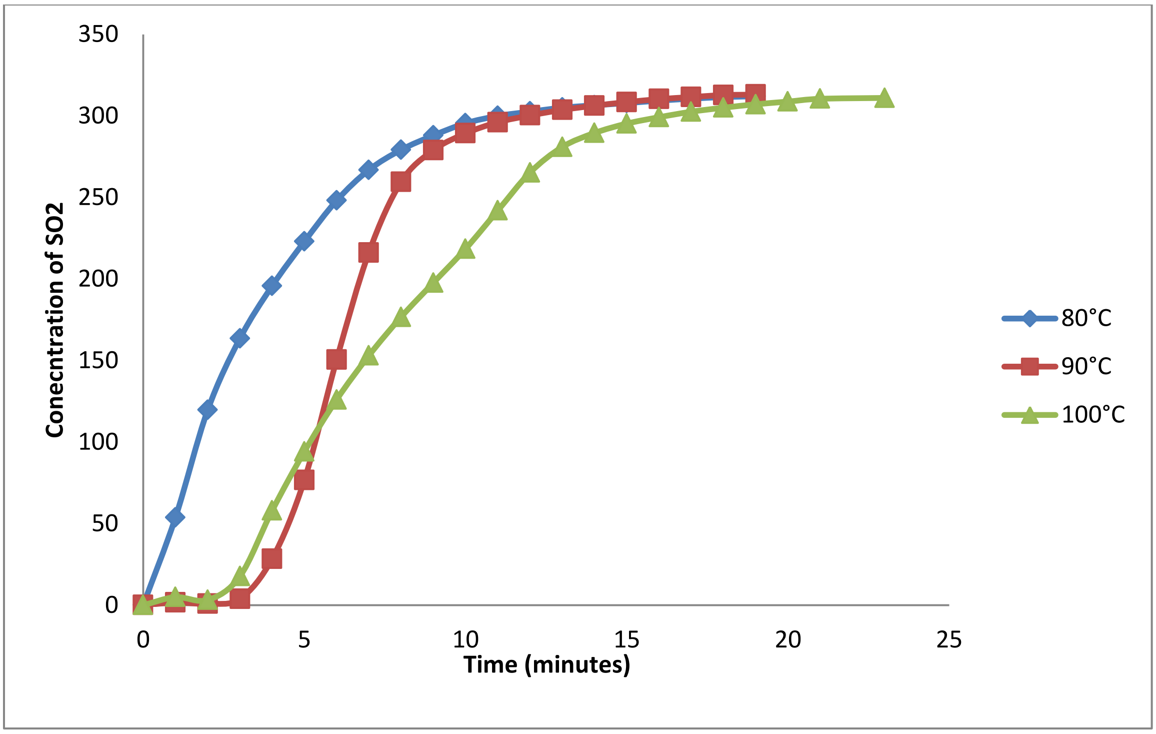

Figure 4.4 The result of eggshell with 10 hour hydration time

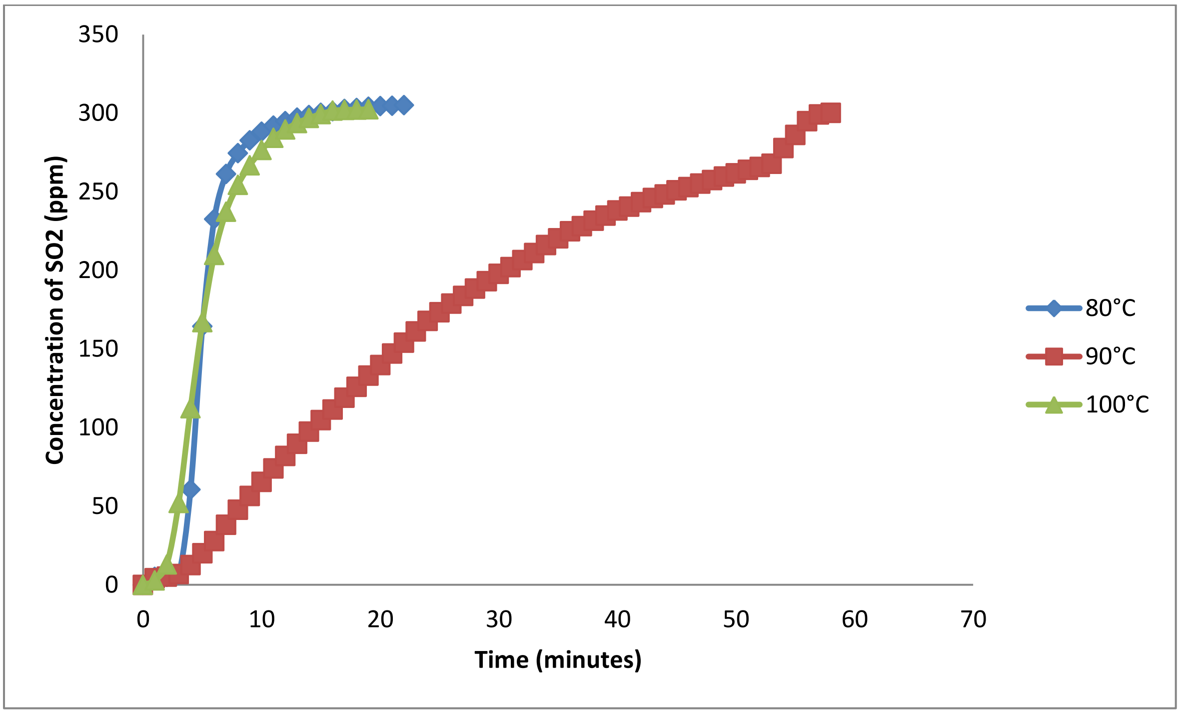

Figure 4.5 The result of eggshell with 30 hour hydration time

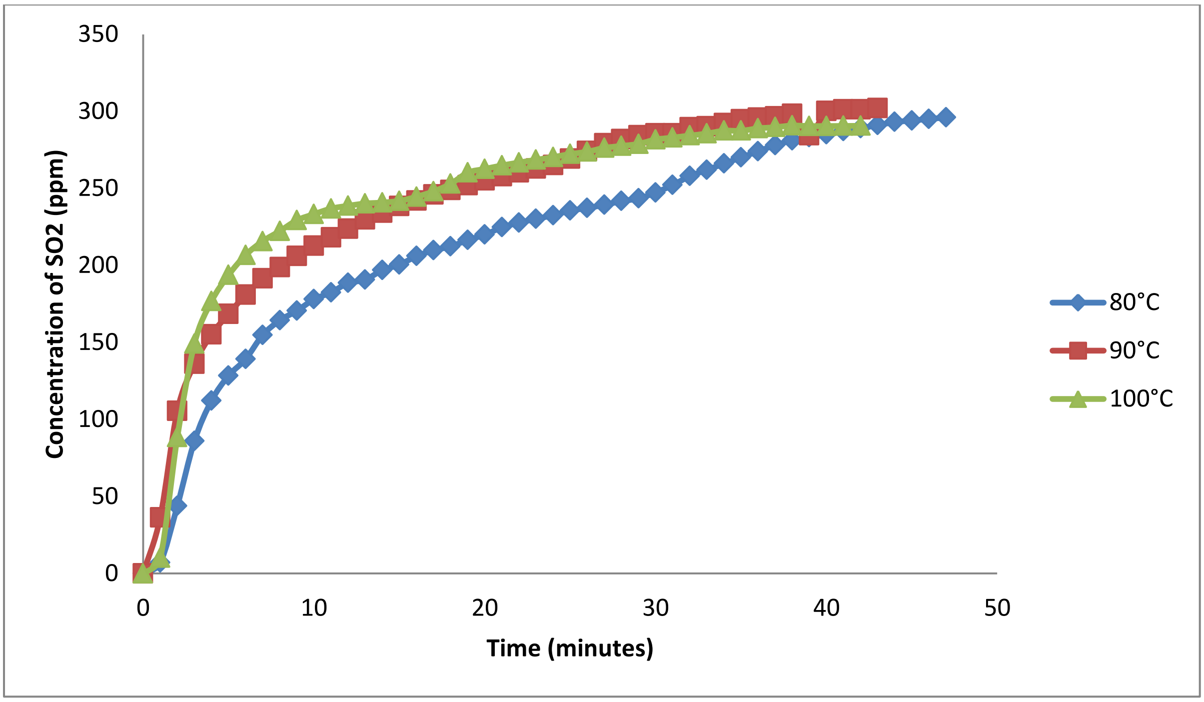

Figure 4.6 The result of CaO with 1 hour hydration time

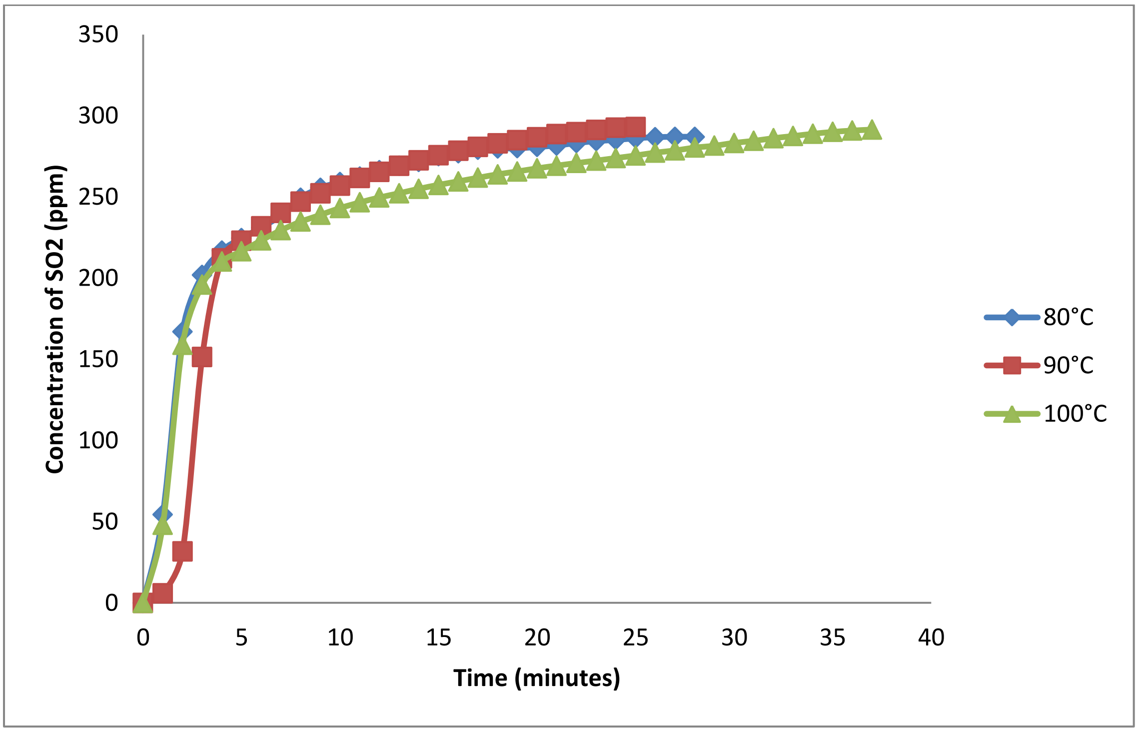

Figure 4.7 The result of CaO with 3 hour hydration time

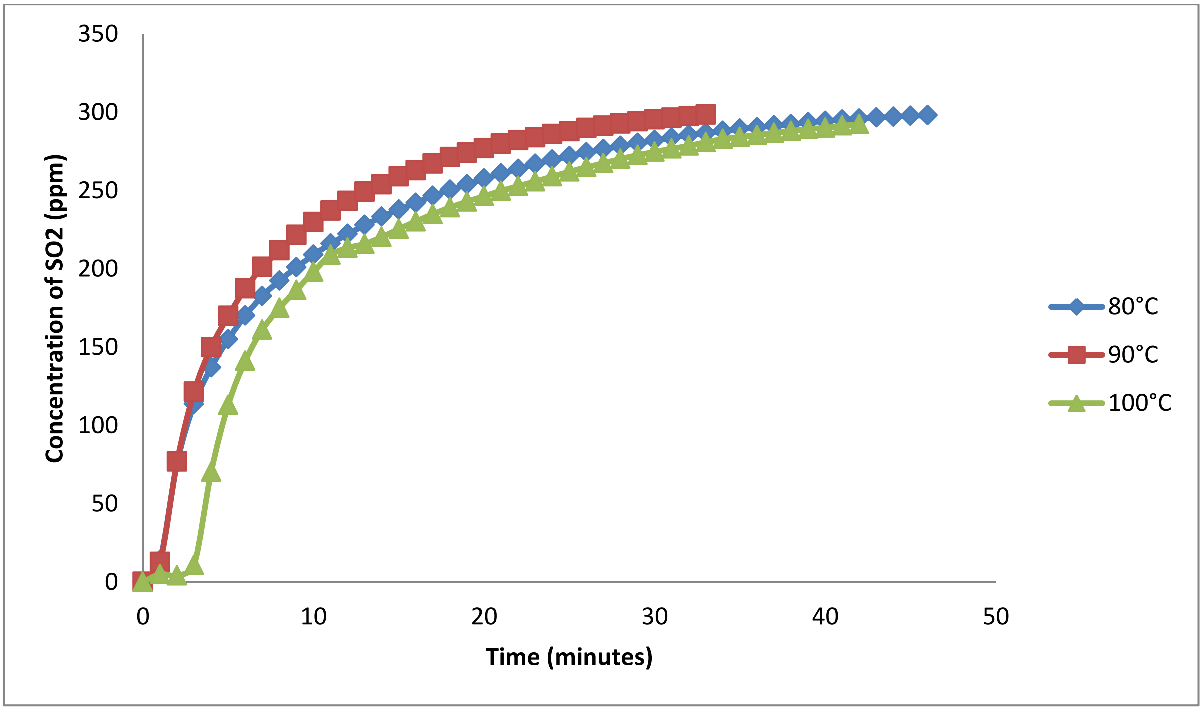

Figure 4.8 The result of CaO with 5 hour hydration time

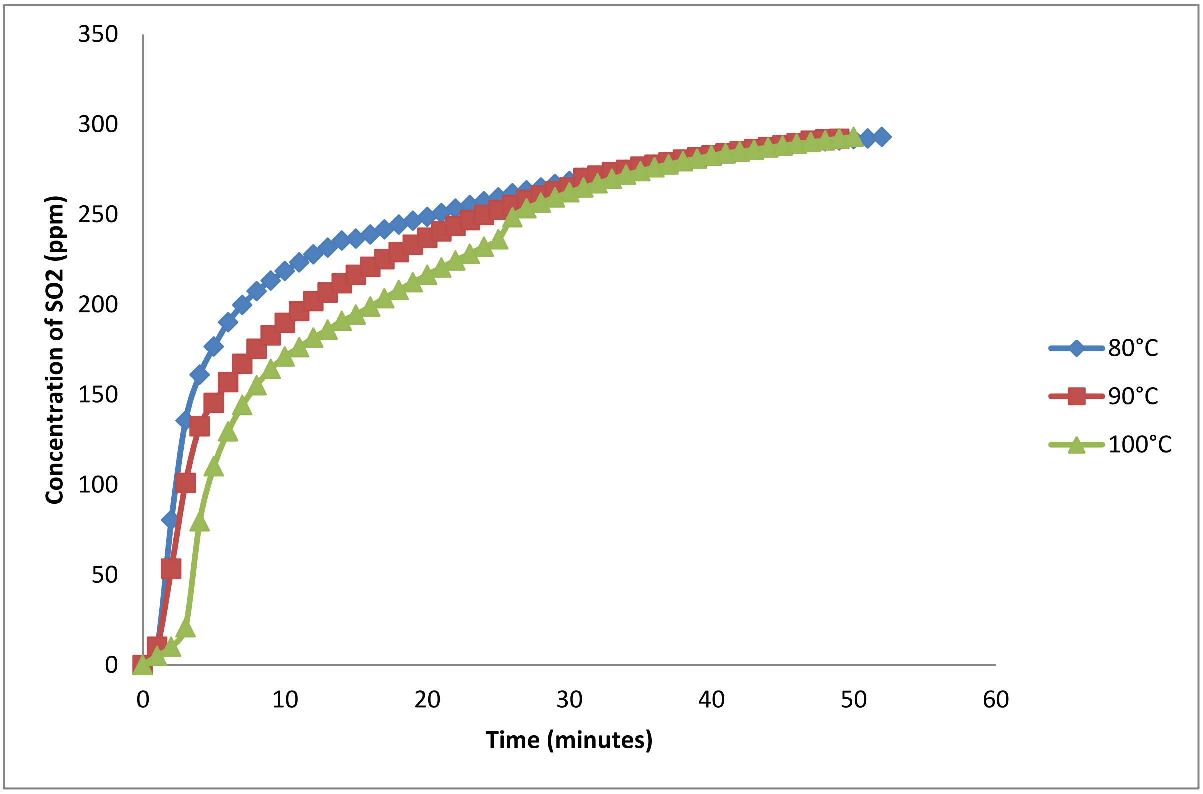

Figure 4.9 The result of CaO with 10 hour hydration time

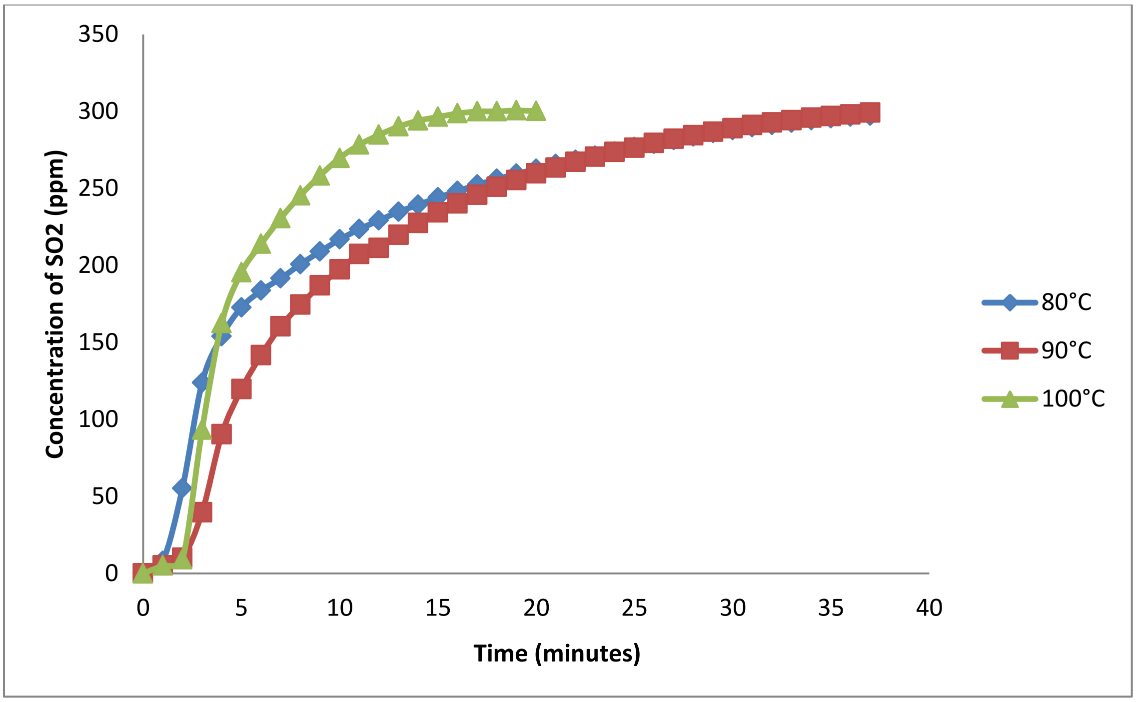

Figure 4.10 The result of CaO with 30 hour hydration time

4.2 Adsorption capacity

Table 4.1 and table 4.2 shows the adsorption capacity and the design parameter of the eggshell and commercial calcium oxide. The highest adsorption capacity for eggshell sample is eggshell labeled A1 with 30 hour hydration time and 90°C hydration temperature with adsorption capacity 1.34 gram SO_2 per gram of eggshell. Contrary to that, the lowest adsorption capacity for eggshell sample can be found at eggshell labeled A3 with 1 hour hydration time and 100°C hydration temperature with adsorption capacity of 0.208 gram SO_2 per gram of eggshell. On the other hand, the best adsorption capacity for commercial calcium oxide sample can be found in CaO labeled A1 with 1 hour hydration time and 80°C hydration temperature. In contrary, the lowest adsorption capacity for commercial calcium oxide can be found in CaO labeled B1 with 3 hour hydration time and 80°C hydration temperature.

For eggshell with 1 hour hydration time, it can be found that the adsorption capacity decrease when the hydration temperature increased. This means that increase in hydration temperature when the hydration time is 1 hour will cause the adsorption capacity to drop. This is the same for eggshell with 5 hour hydration time. But however, at eggshell at 3 hour hydration time shows decrease and increase of adsorption capacity as hydration temperature increases. And eggshell with 10 hour hydration time shows increase in adsorption capacity as hydration temperature increase. There are a few factors that may affect the adsorption capacity such as the surface area exposed to the adsorbate. Every sample has different shape and size which causes the adsorption area to differ hence causing result to be less accurate. Some took longer contact time in order for the adsorption to be more complete, but it does not affect the adsorption capacity. (Armenante, 2014)

Table 4.1 The adsorption capacity and the design parameter of the eggshell

Eggshell Label Code	**Hydration Time, hr**	**Temperature, °C**	**Adsorption Capacity, g_{so2}/g_{es}**
A1	1	80	1.340
A2	1	90	0.217
A3	1	100	0.212
B1	3	80	0.475
B2	3	90	0.415
B3	3	100	1.890
C1	5	80	0.715
C2	5	90	0.613
C3	5	100	0.255
D1	10	80	0.211
D2	10	90	0.425
D3	10	100	0.642
E1	30	80	0.367
E2	30	90	3.936
E3	30	100	0.536

Table 4.2 The adsorption capacity and the design parameter of the CaO

Commercial Calcium Oxide Label Code	**Hydration Time, hr**	**Temperature, °C**	**Adsorption Capacity, g_{so2}/g_{CaO}**
A1	1	80	15.521
A2	1	90	9.425
A3	1	100	4.978
B1	3	80	2.073
B2	3	90	3.046
B3	3	100	3.522
C1	5	80	6.380
C2	5	90	6.099
C3	5	100	10.323
D1	10	80	10.114
D2	10	90	10.639
D3	10	100	12.781
E1	30	80	7.793
E2	30	90	10.139
E3	30	100	4.276

4.3 FTIR spectrum

Commercial calcium oxide and eggshell with the best adsorption capacity and the worst adsorption capacity and their respective original eggshell and original commercial calcium oxide were characterized by Fourier Transform Infrared (FT-IR) in order to determine the functional groups.

For the eggshell with worst adsorption, the FTIR spectrum shows that it consist of two functional groups of aromatics (with C–C stretch (in–ring)), two sharp peak of 1˚, 2˚ amines (N–H wag). For the eggshell with best adsorption, the FTIR spectrum shows that it consists of sharp peak of carboxylic acid (with O–H stretch), sharp peak of alkyl halides (with C–Cl stretch), and alcohol (with O–H stretch, H–bonded) functional groups. The original eggshell consist of sharp peak of alcohol (with O–H stretch, free hydroxyl), nitro compound (with N–O asymmetric stretch), and alkyl halides (with C–Br stretch) functional groups. The original eggshell is lacking of carboxylic acid functional group and with an extra nitro compound functional group compare to the eggshell with best adsorption. On the other hand, the eggshell with worst adsorption shows that it contain of 2˚ amines and aromatics functional group that is not present in the original eggshell nor the eggshell with best adsorption.

On the other hand, CaO with worst adsorption consist of sharp peak of alcohol (with O–H stretch, free hydroxyl), aromatic (with C–C stretch (in–ring)), and alkyl halides (with C–Br stretch) functional groups. The CaO with best adsorption consist of sharp peak of alcohols (with O–H stretch, free hydroxyl), aromatics (with C–C stretch (in–ring)), and alkyl halides. Lastly, the original CaO consist of alcohol (with O–H stretch, free hydroxyl) and alkanes (with C–H bend) functional group. The comparison shown in figure 4.12 shows that the CaO shows that it has similar peak among one another.

It is often found that eggshell consist of carbonate material and amine in the eggshell matrix (Tsai et al, 2005). Also, the O–H stretch shown in FTIR is formed due to residual water. The commercial CaO FTIR wavelength was similar to that of study of calcined calcium carbonate (Witoon, 2011).

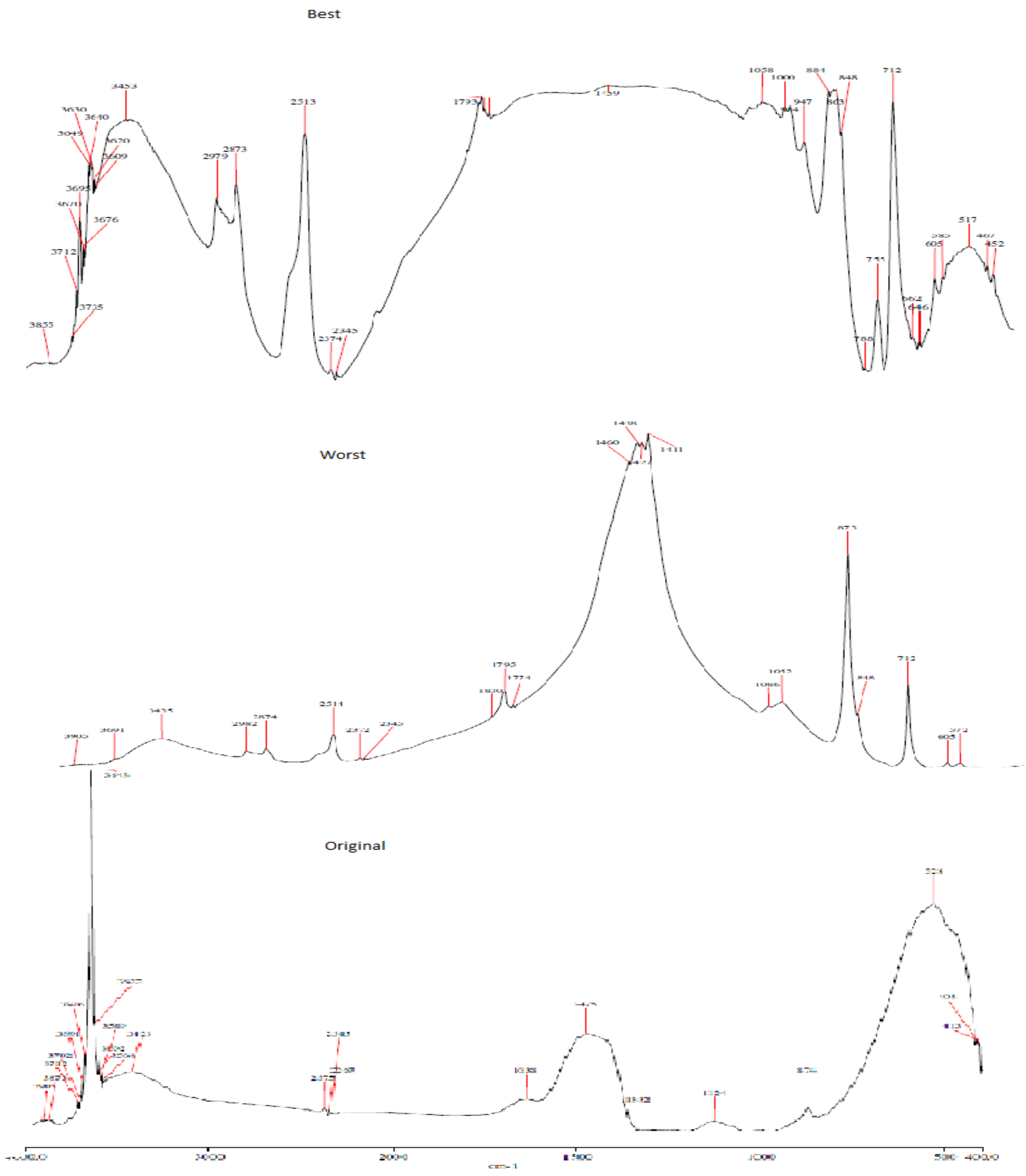

Figure 4.11 The comparison of FTIR spectrum for eggshell

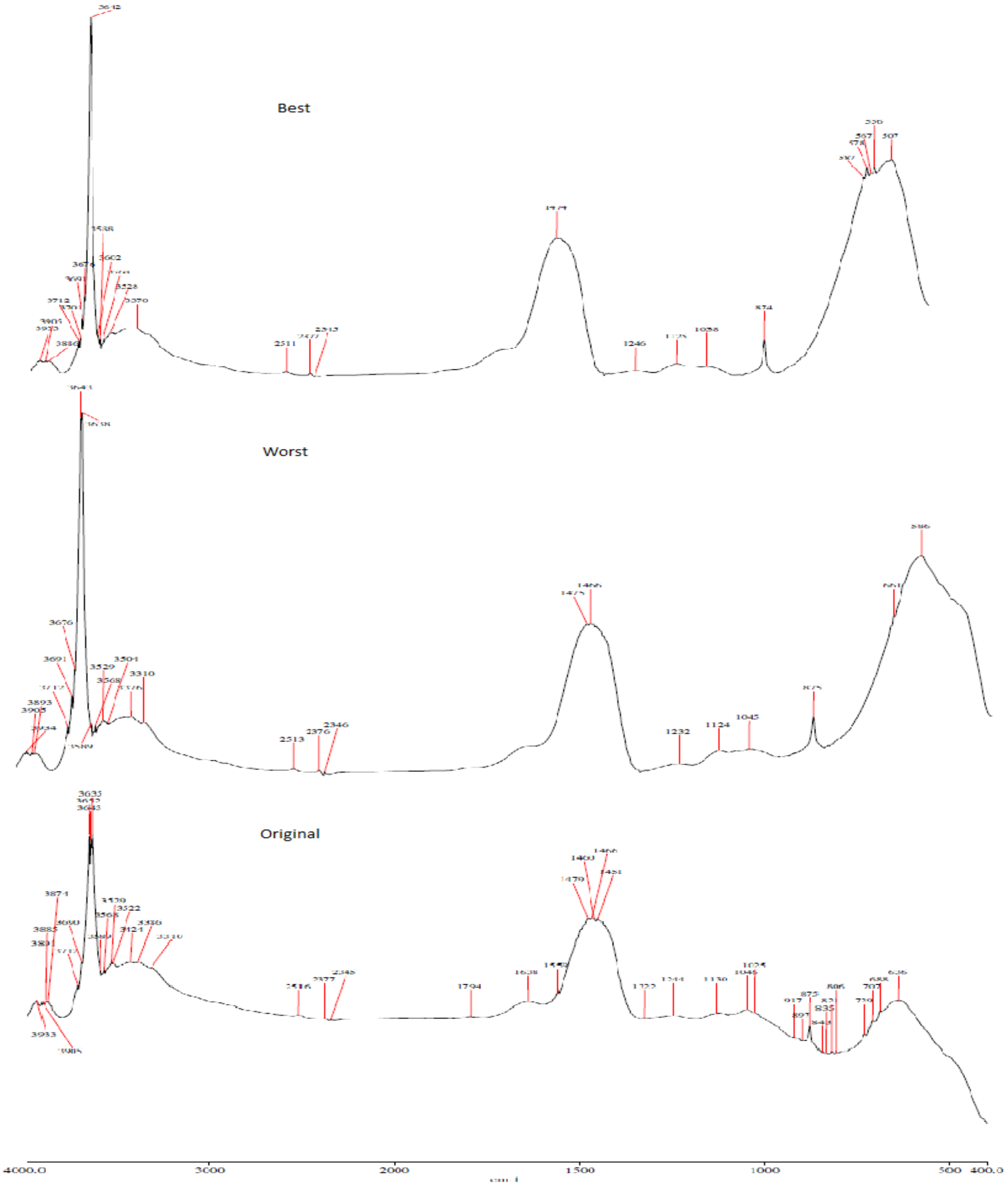

Figure 4.12 The comparison of FTIR spectrum for CaP

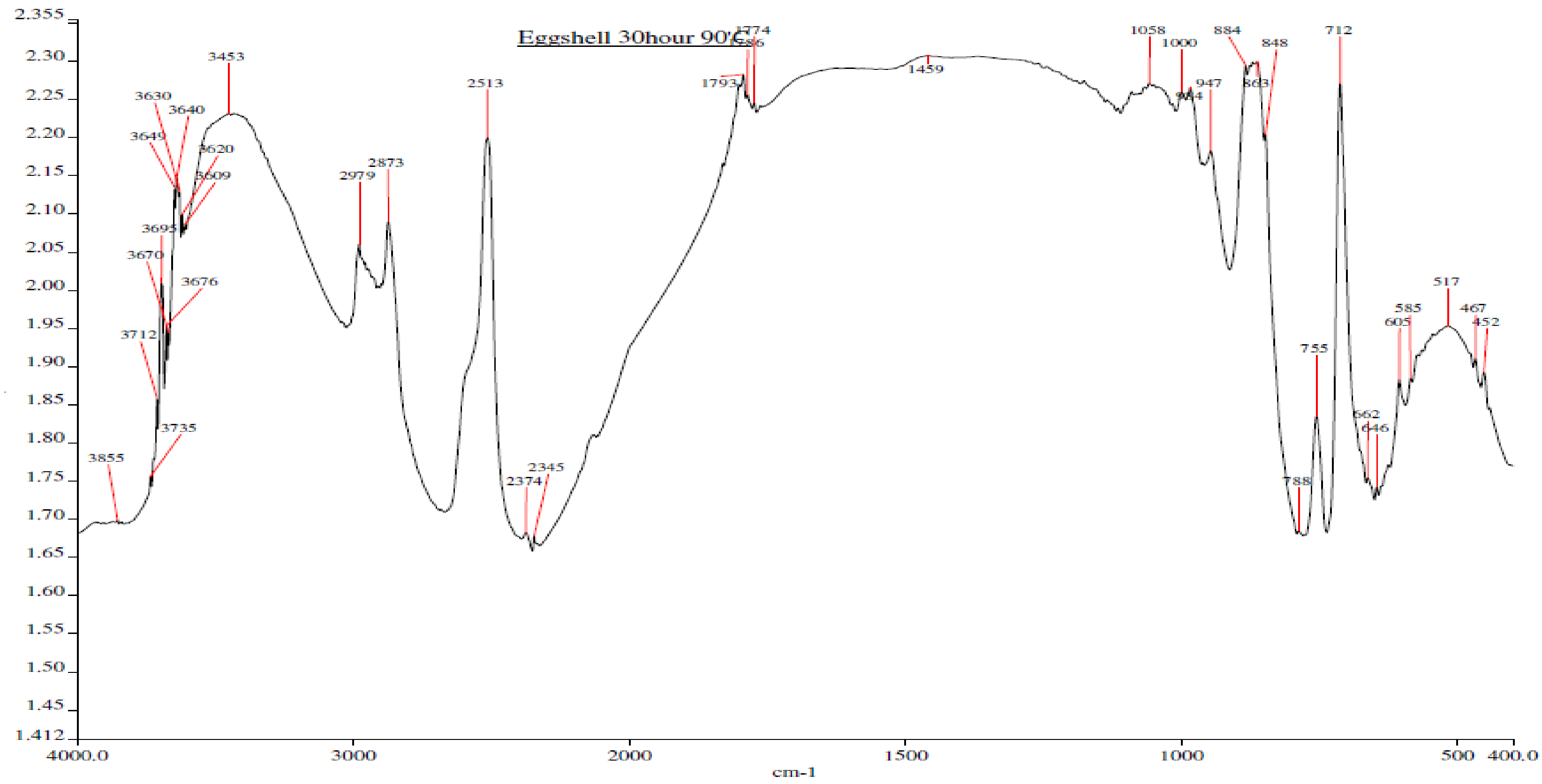

Figure 4.13 FTIR spectrum for eggshell with highest adsorption capacity

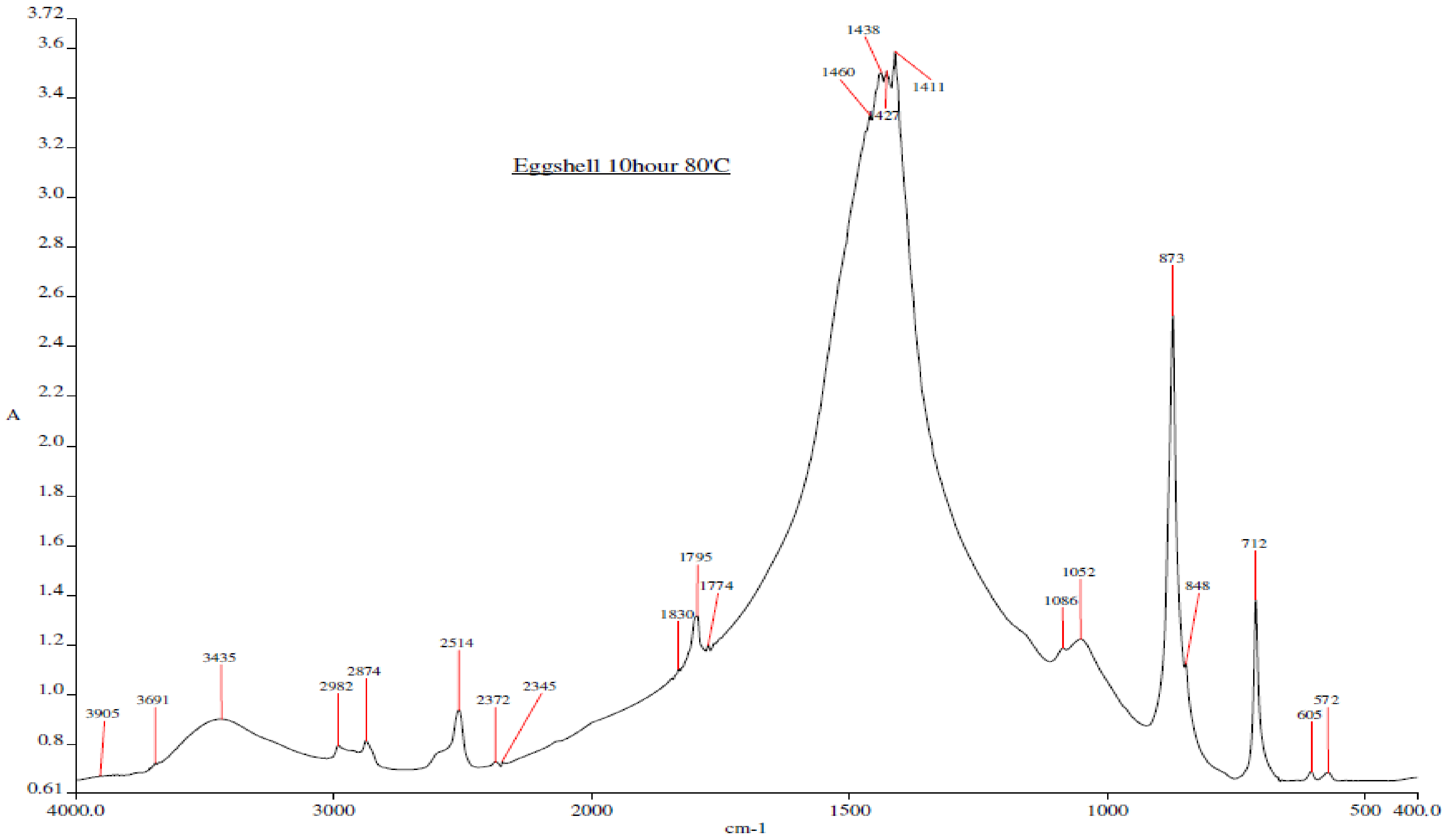

Figure 4.14 FTIR spectrum for eggshell with lowest adsorption capacity

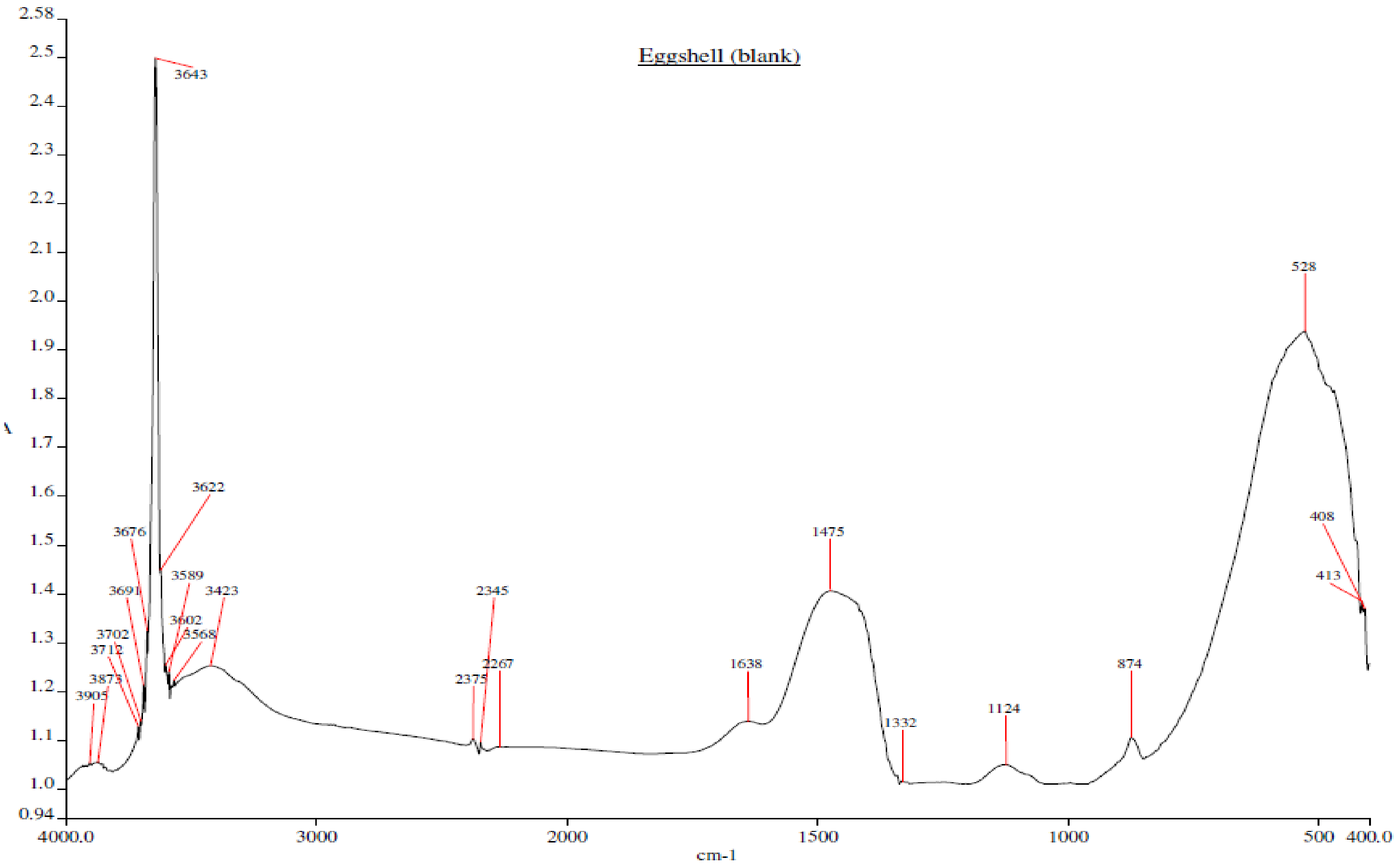

Figure 4.15 FTIR spectrum for blank eggshell sample

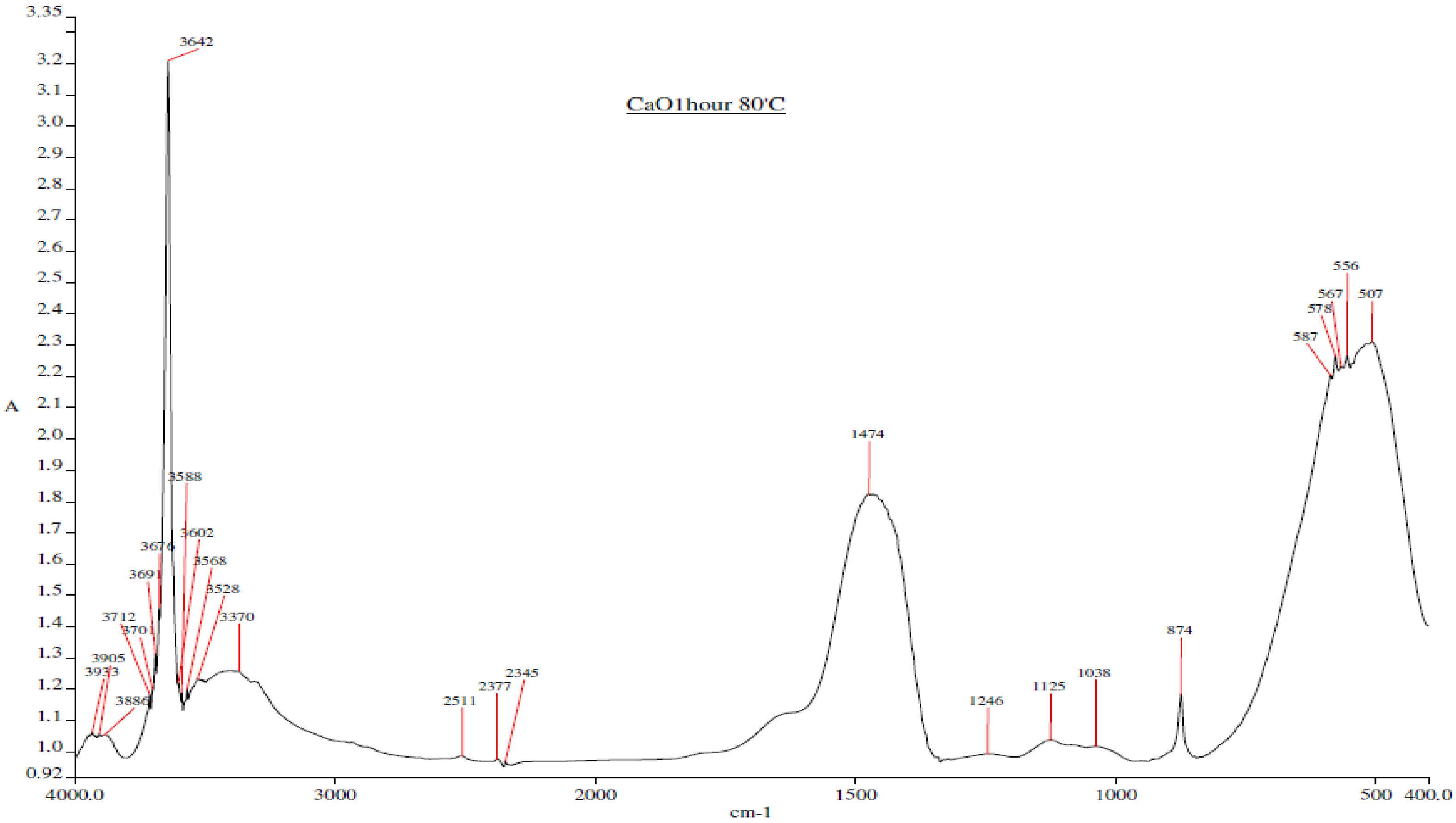

Figure 4.16 FTIR spectrum for CaO with highest adsorption capacity

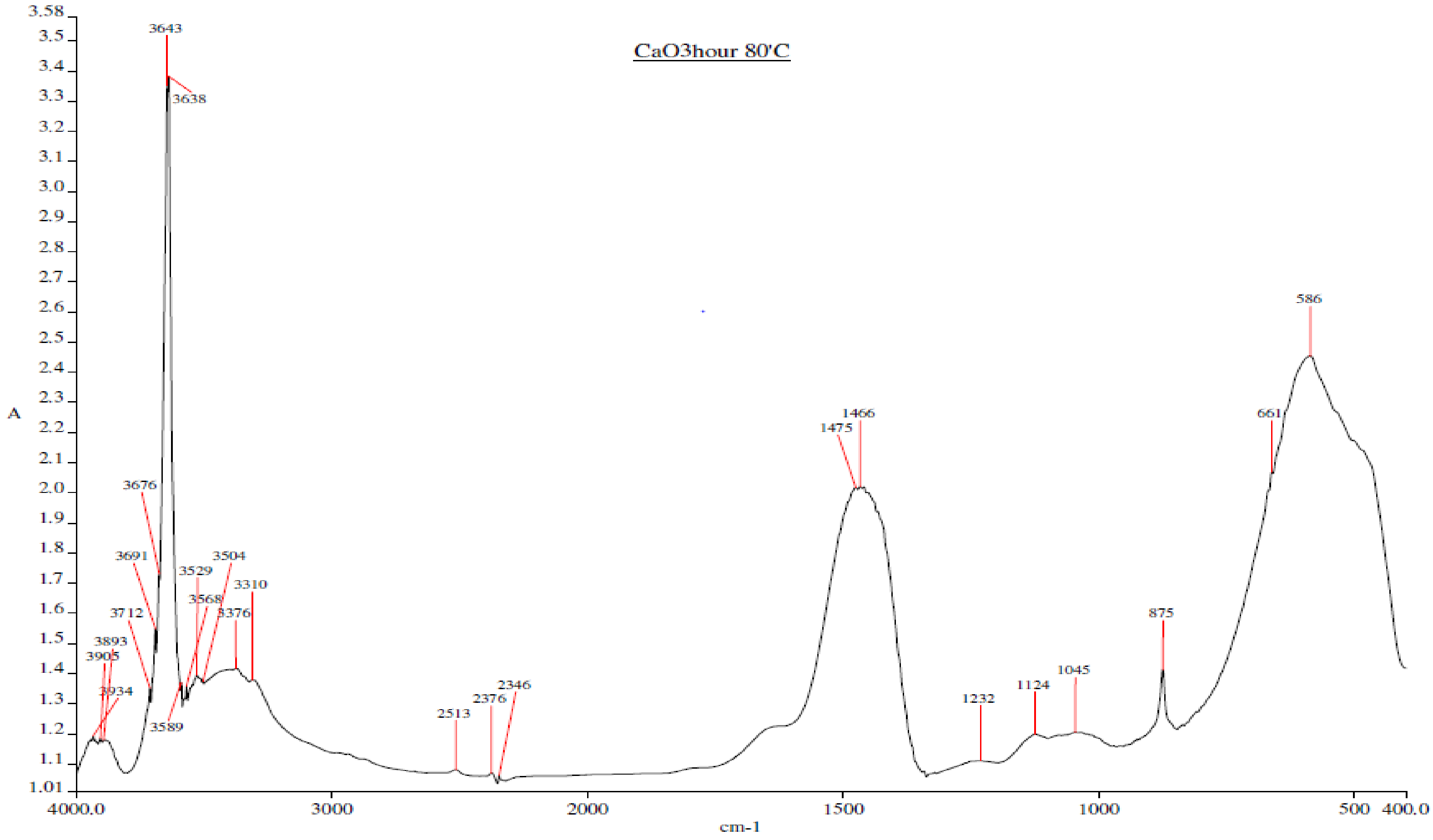

Figure 4.17 FTIR spectrum for CaO with lowest adsorption capacity

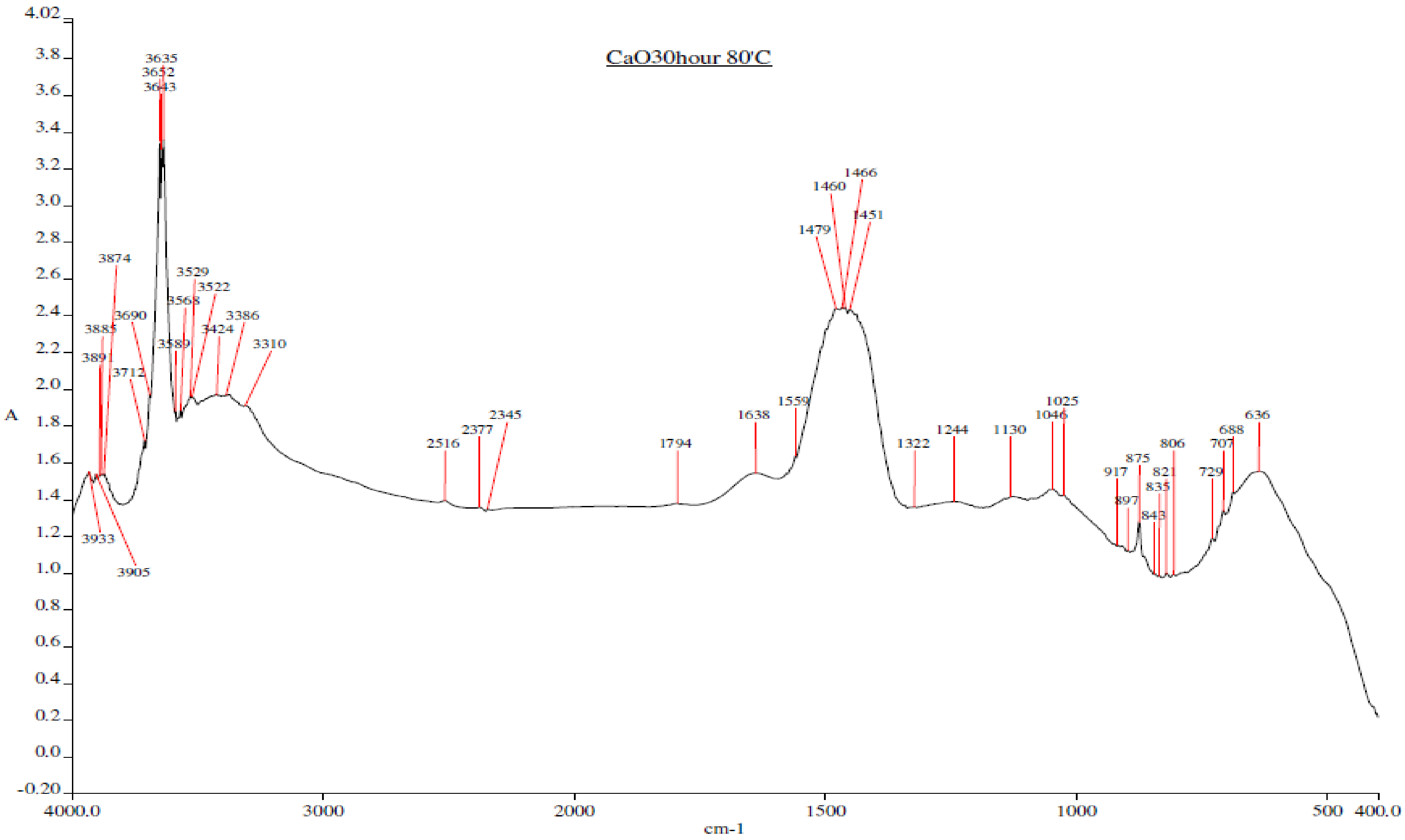

Figure 4.18 FTIR spectrum for original CaO

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This is this study of flue gas desulphurization utilizing waste abundant eggshell. Desulphurization tests using hydrated eggshells and hydrated commercial calcium oxide were carried out and graph of concentration against time were generated by gas analyzer. The graphs generated were used to calculate the adsorption capacity for comparison. After calculation and comparison, it was found that the adsorption capacity of commercial calcium oxide, which is 15.521 g_{so2}/g_{cao} is far higher than the adsorption capacity of eggshell, which is 3.936 $g_{so2}/g_{eggshell}$. Even the eggshell with worst adsorption capacity at 0.211 $g_{so2}/g_{eggshell}$ is still lower than that of commercial calcium oxide at 2.073 g_{so2}/g_{cao}. Therefore further study is required to use eggshell to replace commercial calcium oxide.

5.2 Recommendation

In this study, the results of adsorption capacity were used to conduct the comparison study between commercial calcium oxide and eggshell waste. From the study, it was shown that the commercial calcium oxide has far higher adsorption capacity compare to eggshell waste. So it is further study of eggshell waste is recommended.

There are several factors that could help to improve the study of eggshell desulphurization. Other than just preparing the adsorbent using water hydration, the adsorbent can be prepared with other hydration technique such as steam, alcoholic, and pressurized hydration.

Moreover, instead of only performing FTIR for eggshell characterization, XRD and SEM can be used to further understand the characteristic of the eggshell. Also, parameters such as pH, pressure, and concentration of adsorbent can be used in design of hydration process instead of just temperature and time.

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