



# **Understanding Effect of Process Variables on Extraction of Silica (SiO<sub>2</sub>) from Coal Fly Ash (CFA) and Pulp Waste Ash (PWA)**

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## Candidate's Declaration

I, **Ntombikayise Precious Bhengu**, candidate number **547503**, hereby declare that *The Extraction of Silica from Coal Fly Ash (CFA) and Pulp Waste Ash (PWA) and the Optimization of the Extraction of Silica from CFA* is my own work. This work is being submitted for the Degree of Master of Science in Chemical Engineering to the University of the Witwatersrand, Johannesburg. This work has not been previously submitted for any examination or degree. The work from other authors that has been used in this study has been acknowledged and fully cited as complete references.

Ntombikayise Precious Bhengu

June 6, 2020

Signed:  -----

## Abstract

The disposal of coal fly ash (CFA) and pulp waste (PW) is an environmental problem due to the large amount of it generated. Silica ( $\text{SiO}_2$ ) is contained in CFA and PW is 57.9% and 33.04%, respectively.  $\text{SiO}_2$  is used in the manufacturing of various silica products such as; silica bricks, silica glasses, water extender ( $\text{Na}_2\text{SiO}_3$ ), etc. The commercial production of  $\text{SiO}_2$  is highly energy-intensive, manufactured by smelting quartz at a temperature of 1400 °C. While several studies have been done on  $\text{SiO}_2$  extraction from CFA, none have been done on  $\text{SiO}_2$  extraction from pulp waste ash (PWA). Thus, there are no comparative studies of  $\text{SiO}_2$  extraction between CFA and PWA. Although some studies studied the optimization of  $\text{SiO}_2$  extraction from CFA (Matlob et al., 2012), none studied the optimization of the extraction of silica by studying the four variables, namely; the NaOH concentration, extraction time, NaOH solution to waste ratio, and extraction time. Thus, there is a need of studying the optimization of coal fly ash from coal fly ash. In this study the extraction of  $\text{SiO}_2$  using sol-gel extraction of silica from CFA and PWA is investigated, as well as the optimization of  $\text{SiO}_2$  extraction from CFA. To extract  $\text{SiO}_2$ , PW was first calcinated at 650 °C to form PWA. The two wastes materials (CFA and PWA) were then characterized using; X-Ray Fluorescence (XRF), Scanning Electron Microscopy (SEM) and Thermogravimetric Analysis (TGA).  $\text{SiO}_2$  was extracted from CFA and PWA by treating them with sodium hydroxide (NaOH) and hydrochloric acid (HCl). The extracted  $\text{SiO}_2$  was analyzed using; TGA and SEM. The extraction of  $\text{SiO}_2$  from CFA was then optimized by using the response surface methodology (RSM) approach. Furthermore, to determine whether or not the extraction of  $\text{SiO}_2$  from CFA can be explained with a kinetic model, a kinetic study was done. To perform a kinetic study of  $\text{SiO}_2$  extraction, the optimized extraction conditions were used. The results showed that when  $\text{SiO}_2$  is extracted at 2 M NaOH, 3.5 mL/g NaOH solution to waste ratio, for 45 min at 70 °C in both wastes materials, a silica yield of 10.98% and 37.59% in CFA and PWA is obtained, respectively. The model describing  $\text{SiO}_2$  extraction from CFA was very satisfactory as it gave a  $p$  and  $R^2$  value of 0.0001 and 0.8804, respectively. A  $p$  value  $< 0.05$  indicates that there is less than 5% chance that the model the values represent could be due to noise. An  $R^2$  value close to 1 shows that there is good correlation between the observed and predicted values for  $\text{SiO}_2$  extraction from CFA. About 88.03% of the data can be explained and analyzed by the model. In addition, results of the cross-validation of the model showed an error of about 1%, emphasizing further the validity of the proposed model for  $\text{SiO}_2$  extraction from CFA. The results also showed that the optimum

conditions found for  $\text{SiO}_2$  extraction from CFA using numerical optimization by desirability function were; 86.69 °C, 3 M NaOH, 5 mL/g NaOH solution to waste material ratio and 30 min for  $\text{SiO}_2$  yield of 31.40%. The actual  $\text{SiO}_2$  yield for CFA was 31.06%. The kinetic study results showed that the process of the extraction of  $\text{SiO}_2$  from CFA followed a first-order reaction kinetics. Thus, the encouraging results obtained from this thesis could provide a platform for the beneficiation of these waste material. This would not only lower the amount of PW and CFA that goes into landfills but would subsequently reduce the costs that go into managing the landfills and the energy that is used to manufacture quartz.

Dedicated to my mother  
Grace Ndlovu

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# Nomenclature

## List of Abbreviations

|                                              |                                         |
|----------------------------------------------|-----------------------------------------|
| Al                                           | Aluminum                                |
| Al <sub>2</sub> O <sub>3</sub>               | Aluminum Oxide                          |
| As                                           | Arsenic                                 |
| Ba                                           | Barium                                  |
| B <sub>2</sub> O <sub>3</sub>                | Boron Trioxide                          |
| CFA                                          | Coal Fly Ash                            |
| Ca                                           | Calcium                                 |
| Cr                                           | Chromium                                |
| CaCO <sub>3</sub>                            | Calcium Carbonate                       |
| CaO                                          | Calcium Oxide                           |
| CCD                                          | Central Composite Design                |
| CO <sub>2</sub>                              | Carbon Dioxide                          |
| C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> | Citric Acid                             |
| CH <sub>3</sub> OOH                          | Acetic Acid                             |
| Cr <sub>2</sub> O <sub>3</sub>               | Chromium (III) Oxide                    |
| DF                                           | Desirability Function                   |
| EDS                                          | Energy-Dispersive X-ray Spectroscopy    |
| Fe <sub>2</sub> O <sub>3</sub>               | Iron Oxide                              |
| FTIR                                         | Fourier Transform Infrared Spectroscopy |
| Hg                                           | Mercury                                 |
| H <sub>2</sub> O                             | Water                                   |
| H <sub>3</sub> PO <sub>4</sub>               | Phosphoric Acid                         |
| HF                                           | Hydrofluoric Acid                       |
| HNO <sub>3</sub>                             | Nitric Acid                             |
| H <sub>2</sub> SO <sub>4</sub>               | Sulfuric Acid                           |
| K <sub>2</sub> O                             | Potassium Oxide                         |

|                                   |                              |
|-----------------------------------|------------------------------|
| $\text{Li}_2\text{B}_4\text{O}_7$ | Lithium Tetraborate          |
| Mg                                | Magnesium                    |
| MgO                               | Magnesium Oxide              |
| MnO                               | Manganese Oxide              |
| Na                                | Sodium                       |
| $\text{Na}_2\text{CO}_3$          | Sodium Carbonate             |
| NaOH                              | Sodium Hydroxide             |
| $\text{Na}_2\text{O}$             | Sodium Oxide                 |
| $\text{Na}_2\text{SiO}_3$         | Sodium Silicate              |
| Ni                                | Nickel                       |
| $\text{N}_2$                      | Nitrogen                     |
| O                                 | Oxygen                       |
| $\text{O}_2$                      | Dioxygen                     |
| Pb                                | Lead                         |
| $\text{P}_2\text{O}_5$            | Phosphorus Pentoxide         |
| PW                                | Pulp Waste                   |
| PWA                               | Pulp Waste Ash               |
| RMS                               | Response Surface Methodology |
| SEM                               | Scanning Electron Microscope |
| Se                                | Selenium                     |
| Si                                | Silicon                      |
| $\text{SiO}_2$                    | Silicon Dioxide              |
| $\text{SO}_2$                     | Sulfur Dioxide               |
| TGA                               | Thermogravimetric            |
| V                                 | Vanadium                     |
| $\text{WO}_3$                     | Tungsten Trioxide            |
| XRF                               | X-ray Florescence            |
| Zn                                | Zinc                         |

#### **Units of Measure/ Symbols**

|    |                   |
|----|-------------------|
| Ea | Activation Energy |
|----|-------------------|

|                                             |                              |
|---------------------------------------------|------------------------------|
| $\text{\AA}$                                | Angstrom                     |
| $R^2$                                       | Coefficient of Determination |
| $^{\circ}\text{C}$                          | Degrees                      |
| $^{\circ}\text{F}$                          | Fahrenheit                   |
| $R$                                         | Gas Constant                 |
| $\text{J}\cdot\text{mol}^{-1}$              | Joule Per Mole               |
| $\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$ | Joule Per Mole Kelvin        |
| $\text{K}$                                  | Kelvin                       |
| $k$                                         | Kinetic Constant             |
| $\text{m}^2$                                | Meter Square                 |
| $\mu\text{m}$                               | Micrometer                   |
| $\text{mg}$                                 | Milligram                    |
| $\text{mL}/g$                               | Milliliter Per Gram          |
| $\text{M}$                                  | Molarity                     |
| $\text{nm}$                                 | Nanometer                    |
| $p\text{-value}$                            | Probability value            |
| $\%$                                        | Percent                      |
| $\text{min}^{-1}$                           | Per Minute                   |
| $\text{s}^{-1}$                             | Per Second                   |
| $\text{T}$                                  | Temperature                  |
| $t$                                         | Time                         |

# Chapter 1: Introduction

## 1.1 Introduction

This chapter describes the background, the problem statement, the research aim, questions, objectives, and the significance of this study.

## 1.2 Background and motivation

Waste management is one of the biggest problems facing the industry (Singh et al., 2014). Conventionally, waste management strategies are based on end-pipe technologies. For instance, solid waste such as; sugarcane bagasse waste, rice straw, corn cobs, coal fly ash and pulp waste are taken to landfills. In 2017, South Africa produced about 42 million tons of waste, about 4 million tons of waste was recycled, and about 37 million tons of this waste ended up in landfills (South Africa State of Waste, 2018). The environmental and economic costs of these technologies are high. Therefore, the beneficiation of waste materials such as coal fly ash (CFA) and pulp waste (PW) is of paramount importance. From a financial perspective their beneficiation help save potential cost on treatment of the disposal of waste products and from an environmental perspective, because their use reduces the environmental impact of the new material or product (Federico et al., 2015).

CFA is the byproduct of coal combustion during the manufacturing of electricity in the fired power stations (Yao et al., 2014). About 500 million tons of CFA is produced annually in the world, and is predicted to increase (Matlob et al., 2012). In South Africa 25 million tons of ash is produced annually (Kaduku et al., 2015). Pulp is a soft wet mass of fibres derived from wood or rags. It is used in paper making (Buruberri et al., 2015). The production of paper and paper mill is growing worldwide yearly. In 2013, about 403 million tons of paper was produced resulting to about 179 million tons of pulp being produced (Simão et al., 2018). In the Republic of South Africa there are 21 mill sites ranging from small household tissue mills to the most modern integrated pulp and paper mills, producing approximately 3 million tons per annum of pulp and paper products (Steffen et al., 1990). Both CFA and PW contain heavy metal impurities such as cadmium, mercury and arsenic which are harmful. Improper disposal of CFA and PW can contaminate waterways, ground

water, drinking water and air (Reynolds-Clausen and Singh, 2019). The disposal of CFA and PW in rivers, ponds and sea can also cause harm to aquatic life (Islamia, 2013).

CFA and pulp waste ash (PWA) contain silica ( $\text{SiO}_2$ ), 57.9% and 33.04%, respectively.  $\text{SiO}_2$  is used in the manufacturing of various  $\text{SiO}_2$  products such as; adsorbents, catalyst supports, silica bricks, silica glasses, cement, water extender ( $\text{Na}_2\text{SiO}_3$ ), etc. (Kaduku et al., 2015). Commercially,  $\text{SiO}_2$  is manufactured by sand fusion of high purity silica sand as feedstock. This method is highly energy-intensive, as it requires the reactants to be heated at a temperature of 1400 °C (Yahya et al., 2017). Conventionally, sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) is obtained from silica sand, sodium sulphate is produced as waste. Sodium sulphate requires elaborate treatment before disposal. Another method that is used is the sol-gel process, this method involves high raw materials cost (Gandhi et al., 2015). All these processes involve some or the other disadvantage which increases the cost of production. Silica in agricultural wastes can be extracted using microbial treatment, thermal treatment, or chemical treatment (Permatasari et al., 2016). Thermal treatment of the extraction of  $\text{SiO}_2$  extraction from agricultural wastes involves high temperature in processing of the waste feedstock. This commonly involves the combustion of waste material (Chakraverty et al., 1988; Della et al., 2002; Usman et al., 2014). Chemical treatment involves extraction of silica in agricultural waste by acid leaching or by alkaline leaching. Acids such as;  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  are hazardous to the environment and human and require special disposal treatment which is economically costing (Yahya et al., 2017). Alkaline leaching involves treating the organic waste with an alkaline solvent such as sodium hydroxide to form  $\text{Na}_2\text{SiO}_3$ . To precipitate the  $\text{SiO}_2$ , the  $\text{Na}_2\text{SiO}_3$  is neutralized with an acid (Naddaf et al., 2018). The use of an alkaline solvent to extract  $\text{SiO}_2$  has advantages such as; it can be stored for a long time, it has good adsorption and ion exchange properties, and its characteristics can be adjusted depending on the combustion temperature (quartz, amorphous, cristobalite and tridime) (Setyawan et al., 2019).

Due to the high silica content of the CFA and PWA as well as the high energy intensity of commercially manufacturing  $\text{SiO}_2$ , it is of paramount importance to study the extraction of  $\text{SiO}_2$  from the two wastes materials.  $\text{SiO}_2$  extraction is influenced by several factors. These factors include temperature,  $\text{NaOH}$  concentration,  $\text{NaOH}$  solution to waste ratio and extraction time. These factors to some extent, dictate amount of  $\text{SiO}_2$  that is extracted from the two waste materials.

For example, an increase in temperature results in an increase in the  $\text{SiO}_2$ , at higher temperatures molecules have more thermal energy required for effective reaction (Shermi, 2013). Furthermore, the more the solvent, the higher the contact area, so the distribution of solvent to solid waste will be higher. The even distribution of solvents to solid waste increases the formation of  $\text{Na}_2\text{SiO}_3$  and thus the yield of  $\text{SiO}_2$  (Setyawan et al., 2019). An increase in the extraction time results in an increase in the  $\text{SiO}_2$  yield. A prolonged exposure of the solid waste in the solvent, allows adequate time for desired compounds to migrate into the solvent (Che Sulaiman et al., 2017).

In order to extract a high yield of  $\text{SiO}_2$  with minimum costs, it is important to optimize the extraction process by investigating the interaction process variables, the main effects and the interactive effects using a useful tool for studying the interaction of two or more variables such a response surface methodology (RSM) (Rezazi et al., 2017). RSM is a statistical and mathematical technique for designing experiments, building models, evaluating the relative significance of numerous independent variables, and determining the optimum conditions for desirable responses (Che Sulaiman et al., 2017; Matori et al., 2009; Rezazi et al., 2017). Previous studies on the optimization of extraction dealt with the classical method of experimentation (Matlob et al., 2012). This method involves changing one of the independent extraction parameters while maintaining the others at fixed level. This method is extremely time consuming as it involves the need of many experimental runs. It also ignores the interaction between the considered operating parameters which results to a low efficiency in optimization. Statistical methods such as RSM do not only help optimize the extraction method, but they also reduce the total experimental runs, resulting in saving resources and time (Pandey et al., 2016). The central composite design (CCD) and the Box-Behnken design (BBD) are the two most common designs used extensively in RSM. CCD is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusual large number of designs (Chitsiga et al., 2018).

While several studies have been done on  $\text{SiO}_2$  extraction from CFA (Font et al., 2009; Kaduku et al., 2015; Music et al., 2012; Sedres, 2016), none have been done on  $\text{SiO}_2$  extraction from PWA. Thus, no comparative studies on the extraction of  $\text{SiO}_2$  from CFA and PWA.

This research, therefore, is focused on using sol-gel processes using as minimum costs and energy as possible to extract  $\text{SiO}_2$  from CFA and PWA. Its main focus was to determine which waste material is the best source of silica, by determining which one extracts the highest yield of  $\text{SiO}_2$  at the same extraction conditions. This study also focused on establishing the optimum extraction conditions of  $\text{SiO}_2$  from CFA and whether or not  $\text{SiO}_2$  extraction from CFA can be explained using a kinetic model.

### **1.3 Problem statement**

The disposal of coal fly ash and pulp waste is an environmental problem due to the large amount generated. About 500 million tons of CFA and about 179 million tons of pulp waste is produced annually in the world (Matlob et al., 2012; Simão et al., 2018). Improper disposal of CFA and PW can contaminate waterways, ground water, drinking water and air (Reynolds-Clausen and Singh, 2019). The disposal of CFA and PW in rivers, ponds and sea can also cause harm to aquatic life (Islamia, 2013). 57.9% and 31.60% of silica is contained in CFA and PW, respectively (Kaduku et al., 2015; Vassilev et al., 2013).  $\text{SiO}_2$  is used in the manufacturing of various silica products such as; adsorbents, catalyst supports, silica bricks, silica glasses, cement, water extender ( $\text{Na}_2\text{SiO}_3$ ), etc. (Buruberri et al., 2015; Kaduku et al., 2015; Sharma, 1997). Commercially, silica is manufactured by sand fusion of high purity silica sand as feedstock. This method is highly energy-intensive, as it requires the reactants to be heated at a temperature of 1400 °C (Yahya et al., 2017). Conventionally, sodium silicate is obtained from silica sand, sodium sulphate is produced as waste. Sodium sulphate requires elaborate treatment before disposal. Another method that is used is the sol-gel process, this method involves high raw materials cost (Gandhi et al., 2015). This study looks at using sol-gel processes using as minimum costs as possible. All these processes involve some or the other disadvantage which increases the cost of production. Silica in agricultural wastes can be extracted using chemical treatment, thermal treatment, or microbial treatment (Permatasari et al., 2016).

Although several studies have been done on  $\text{SiO}_2$  extraction from CFA (Font et al., 2009; Kaduku et al., 2015; Music et al., 2012; Sedres, 2016), none have been done on  $\text{SiO}_2$  extraction from PWA. Thus, hence no comparative studies between coal fly ash and pulp waste of the extraction of  $\text{SiO}_2$  have been done. Although some studies studied the optimization of  $\text{SiO}_2$  extraction from CFA

(Matlob et al., 2012), none studied the optimization of the extraction of silica by studying the four variables, namely; the NaOH concentration, extraction time, NaOH solution to waste ratio, and extraction time. Thus, there is a need of studying the optimization of coal fly ash from coal fly ash.

## **1.4 Research aim, questions and objective**

### **1.4.1 Research aim**

The aim of this study is to extract  $\text{SiO}_2$  from two South African wastes, CFA and PWA using the most cost effective and environmentally friendly method and optimize the  $\text{SiO}_2$  extraction from CFA.

### **1.4.2 Research questions**

The following research questions were addressed during the course of this study:

- What is the chemical composition of the two waste materials?
- Can  $\text{SiO}_2$  be successfully extracted from the two waste materials using the same extraction conditions?
- What will the effect of extraction conditions on the yield and quality of  $\text{SiO}_2$  extracted from CFA?
- Can the yield of  $\text{SiO}_2$  obtained from CFA be optimized?
- Can the rate of extraction of silica from CFA be explained with a kinetic model?

### **1.4.3 Research objectives**

To proffer solution to the above research questions, the following research objectives were considered:

- To characterize the CFA and PWA
- To extract  $\text{SiO}_2$  from both CFA and PWA using the same extraction conditions
- To investigate the effect of variables such as (temperature, time and NaOH/waste material ratio) on the extraction process and optimize the process
- To do a kinetic study of the extraction of  $\text{SiO}_2$  from CFA and get a kinetic model to describe it

### **1.5 Research contribution to knowledge**

The management of the disposal of waste is an environmental problem. In 2017, about 42 million tons of waste was generated, only 4 million tons of this waste was recycled, and the remaining 38 million tons of waste ended up in landfills (South Africa State of Waste, 2018). Most of the waste that ends up in the landfills is toxic to the environment. For example, coal fly ash and pulp waste contain harmful metals which when coming into contact with the environment may cause harm (Kaduku et al., 2015; Vassilev et al., 2013). So, there are strict legislations put with the management of the landfills where these materials are disposed. The management of these landfills is expensive (Singh et al., 2014). Coal fly ash and pulp waste also contain silica which is manufactured by melting quartz and is highly energy intensive (Kaduku et al., 2015; Vassilev et al., 2013). The industrial manufacturing of  $\text{SiO}_2$  also uses large amount of acids that generate large amount of effluents and greenhouse gases (Fernandes et al., 2017). Thus, the beneficiation of these waste materials will not only lower the amount of PW and CFA that goes into landfills, but it will also reduce the costs that goes into managing the landfills and the energy that is used to manufacture quartz.

### **1.6 Scope of the research and dissertation layout**

The extraction of  $\text{SiO}_2$  from CFA has been studied by many researchers (Font et al., 2009; Kaduku et al., 2015; Music et al., 2012; Sedres, 2016), no studies have been done on the  $\text{SiO}_2$  extraction from PWA. This work was only limited on the extraction of  $\text{SiO}_2$  from South African CFA and PWA, as well as the optimization of  $\text{SiO}_2$  extraction from CFA. The scope of this work was to characterize the two waste materials using different characterization techniques, extract  $\text{SiO}_2$  from CFA and PWA, optimize  $\text{SiO}_2$  extraction from CFA and determine if the  $\text{SiO}_2$  extraction from CFA can be explained using a kinetic model. This report is divided into seven eight:

**Chapter 1:** This chapter describes the background, the problem statement, the research aim, questions, objectives, and the significance of this study.

**Chapter 2:** This chapter provides information on the basic concepts in this study such as CFA, PW, silica, methods of silica production, optimization methods, kinetics of silica production and uses of silica.

**Chapter 3:** This chapter describes the material and experimental procedures employed for the extraction of  $\text{SiO}_2$  from CFA. This chapter also gives the description of the optimization of the extraction of  $\text{SiO}_2$  from CFA and the kinetic study of the extraction of  $\text{SiO}_2$  from CFA.

**Chapter 4:** This chapter discusses the results obtained from the characterization of South African coal fly ash and pulp waste ash using TGA XRF and SEM.

**Chapter 5:** This chapter discusses the results obtained for the extraction of Silica from coal fly ash and pulp waste ash

**Chapter 6:** This chapter discusses the results obtained for the effect of the operating variables on the extraction of  $\text{SiO}_2$  from CFA, as well as the optimization results, using response surface methodology (RSM) approach.

**Chapter 7:** This chapter discusses the results obtained for the kinetic study of the extraction of  $\text{SiO}_2$  from CFA.

**Chapter 8:** This chapter gives a brief summary of the findings in this study with general conclusions and recommendations for future research work.

## Chapter 2: Literature Review

### 2.1 Introduction

This chapter provides information on the basic concepts in this study such as CFA, PW, silica, methods of silica production, optimization methods, kinetics of silica production and uses of silica.

### 2.2 Coal fly ash

CFA is an industrial by-product generated from a coal combustion process in thermal power plants. To supply the bulk of South Africa with electricity, coal-fired power stations of Eskom use 120 million tons of coal per year, producing 25 million tons of ash (Eskom, 2016). CFA is one of the most complex and abundant of anthropogenic materials (Yao et al., 2014). It comprises of powdery particles which are mostly spherical in shape, either hollow or solid, and predominantly amorphous in nature. The particle size is less than a 0.001 to 200  $\mu\text{m}$ . The specific gravity of CFA ranges between 2.1 and 3.0. Its specific surface area varies between 170 and 1000  $\text{m}^2$ . The colour of fly ash vary from tan to grey to black, this depends on the amount of unburnt carbon (Ahmaruzzaman, 2010). CFA contains aluminum (Al), calcium (Ca), magnesium (Mg), iron (Fe), sodium (Na) and silicon (Si) as predominant elements. It also contains a large amount of metals namely; arsenic (As), barium (Ba), mercury (Hg), chromium (Cr), nickel (Ni), vanadium (V), lead (Pb), zinc (Zn) and selenium (Se) which are toxic to the environment (Lokeshappa and Anil, 2012). Its characteristics depend on the source of coal used in the power plant and the method of combustion. Table 2-1, adapted from Nelson et al. (1990), shows that CFA can be categorized as either pozzolanic (F) or cementitious (C). The pozzolanic CFA is labeled as class F, which contains about 70 percent of  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ . For the cementitious CFA (C), and it contains about 50 percent of  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  (Landman, 2003). Coal based thermal power plants contribute about 39% of the total amount of electricity generated throughout the world, they are one of the biggest sources of electricity. This is because coal is the most abundant fossil fuel, and it is also cheaper than other fuels such as natural gas and oil (Sahoo et al., 2016). The disposal of CFA is a worldwide concern, thus converting it into useful materials instead of disposing it into landfills is important (Zhang et al., 2017). CFA contains 57.9% of  $\text{SiO}_2$  (Kaduku et al., 2015). Since CFA is rich in silica ( $\text{SiO}_2$ ), it can be used as source of  $\text{SiO}_2$  which is a vital element for materials which have plenty of uses in the industry and those which are used in our daily life.

Table 2-1: Classification of fly ashes

| <b>Mineral Admixture Class</b>                          | <b>F</b> | <b>C</b> |
|---------------------------------------------------------|----------|----------|
| SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub> min % | 70       | 50       |
| SO <sub>3</sub> , max %                                 | 5        | 5        |
| Moisture content, max %                                 | 3        | 3        |
| Loss on ignition, max %                                 | 12       | 6        |

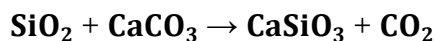
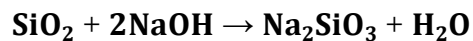
### 2.3 Pulp waste

Pulp is made from fibres from trees and other plant materials. Materials made from wood pulp are; crayon, diapers, cellulose acetate, and cellulose esters, which are used for explosives, packaging film, and cloth. Pulp is a soft wet mass of fibres derived from wood or rags, used in paper making. Pulp paper wastes are mostly used in energy production and agriculture, for building materials. The sludge is considered as a substitute for fertilizer as it improves the biological, physical and chemical properties of the soil (Buruberri et al., 2015). Paper making industry and cellulose generate a lot of waste material. The paper and pulp industry is characterized by four key processes, namely; chemical pulping, mechanical and chemi-mechanical pulping, recycled fibre processing and paper making processes. Residues and by-products from chemi-mechanical pulping and mechanical pulping include straw, wood and reed residues, excess sludges, fiber and rejects. The recycling of cardboard waste and paper in industrial production of cellulosic pulp packaging is broadly significant for socio-economical and industrial point of view. Recycling of pulp waste leads to the conservation of forest resources, to a decrease in the industrial solid waste and a decrease in the need for incinerations (Federico et al., 2015). The different types of processes in the paper and pulp industry result in the development of different solid waste and sludge. The solid waste from the production of pulp and the paper mill operations contain a few organic compounds. These organic compounds are in a form of recycled paper fibres or wood, pathogens and chlorinated compounds, a large amount of quantity trace elements and ash (Monte et al., 2009). Pulp paper wastes contain a small amount of oxides; SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, which can be used for all the clinker productions (Buruberri et al., 2015). SiO<sub>2</sub> contained in PW varies, pulp waste investigated by Vassilev et al. (2013) contained 31.60%. Since pulp waste is rich in SiO<sub>2</sub>, it can be used as source of SiO<sub>2</sub> which is a vital element for materials which have plenty of uses in the industry and those which are used in our daily life.

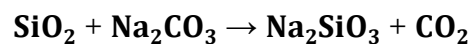
## 2.4 Silicon dioxide (SiO<sub>2</sub>)

Silicon dioxide (SiO<sub>2</sub>) is a crystalline solid which occurs in nature in a form of amorphous silica (flint, opal, hydrated silica, and precipitated chalk), crystalline silica (quartz, quartzite, sandstone, sand, rock crystal etc.) and as cellular silica (diatomite, tripole, ransanite, etc) (Sharma, 1997). Each silicon (Si) atom is surrounded by a tetrahedral array of oxygen (O) atoms (Atkins et al., 2009). For all silica, all the Si atoms are surrounded tetrahedrally by four O atoms. Each oxygen atom is shared with another tetrahedron, making the molecule to have an average stoichiometry of SiO<sub>2</sub>. Si and O are the two most common elements in the earth's crust, together they constitute of 83.77 atom % and 74.32 weight % of crystal rocks, and this is why it is not surprising that SiO<sub>2</sub> is one of the most abundant oxides on the earth's crust. SiO<sub>2</sub> is formed when Si is exposed to O<sub>2</sub> (or air). When Si is exposed to air at ambient temperature, a thin layer of approximately 1nm or 10 Å is formed on the surface. To grow well, controlled layers of SiO<sub>2</sub> higher temperatures (600 °C - 1200 °C) and alternative environments are used. This is done by using wet or dry oxidation with H<sub>2</sub>O and O<sub>2</sub>, respectively. The depth of the layer of Si replaced by the dioxide is 44% of depth of the SiO<sub>2</sub> layer produced (Gandhi et al., 2015).

There are three different crystalline forms of SiO<sub>2</sub>, each of which has a low and a high temperature modification (Kumar De, 2003). All types of silica are insoluble in water; they resist the action of all acids except hydrofluoric acid which readily acts on it, producing silicon tetrafluoride. When silica reacts with alkalis, alkaline earths and their carbons, it forms silicates since it is acidic in nature.



When pure sand (silica) is fused with sodium carbonate, sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) is formed.



The fused mass is broken up and heated with water under pressure in an autoclave when it dissolves to form a thick solution known as water glass. This is the reason why sodium silicate has the trade name “*water glass*” (Kumar De, 2003).

SiO<sub>2</sub> is contained in different waste materials such as rice husk ash, rice straw, corn cobs, bagasse, pulp waste ash, coal fly ash and a lot more (Permatasari et al., 2016). This occurrence of SiO<sub>2</sub> in man’s immediate surrounding is motivation why there is research focusing of different techniques of extraction of SiO<sub>2</sub> from wastes materials (Gandhi et al., 2015).

## **2.5 Conventional method of manufacturing SiO<sub>2</sub>**

Manufacturing of SiO<sub>2</sub> commercially is based on mechanical, physical and is highly energy intensive thermal operations at high temperatures using a large amount of acids, generating a large amount of effluents and greenhouse gases (Fernandes et al., 2017). When SiO<sub>2</sub> is manufactured at an industrial scale it is required that the reactants be heated as high as 1400 °C. SiO<sub>2</sub> is manufactured by the sand fusion of high purity SiO<sub>2</sub> sand as the feedstock. To produce SiO<sub>2</sub>, Sodium silicate is first manufactured by using the State-of-Art Technology. Pure silica sand is fused with Soda ash in Rotary furnace at 1300 °C, resulting in various SiO<sub>2</sub>/Na<sub>2</sub>O ratios being produced. A clear glass of sodium silicate is produced when the mold cools down. Silica precipitates when the sodium silicate undergoes acid precipitation. Through this method of the production of SiO<sub>2</sub>, sodium sulphate is generated as waste product, which is hard to manage, as it requires elaborate treatment to meet emission standards. The process requires effluent treatment for sodium sulphate. This makes the process expensive and if not treated well, it will contribute to environmental pollution (Gandhi et al., 2015).

## **2.6 Methods of Extraction of SiO<sub>2</sub> from Agricultural Waste**

Chemical treatment, thermal treatment, and microbial treatment are methods used for the extraction of SiO<sub>2</sub> from agricultural wastes (Permatasari et al., 2016).

Chemical treatment involves extraction of silica in agricultural waste by acid leaching or by alkaline leaching. Leaching is an extraction of certain materials from a carrier into a liquid or removes the impurities of the materials by dissolving them away from the solids (Matori et al.,

2009). Acid leaching involves a pretreatment of the organic waste with an acid such as hydrochloric acid (HCl), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and, nitric acid (HNO<sub>3</sub>), to remove metal impurities such as aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) and CaO, this also helps improve the purity of the SiO<sub>2</sub> in the waste material (Kaduku et al., 2015; Permatasari et al., 2016). The pretreated waste is then reacted with sodium hydroxide (NaOH) to form sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>). The sodium hydroxide is then neutralized with an acid to precipitate SiO<sub>2</sub> (Matori et al., 2009; Adam et al., 2011; Selvakumar et al., 2014; Kaduku et al., 2015). Acids such as; HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> are hazardous to the environment and human and require special disposal treatment which is economically costing (Yahya et al., 2017). Alkaline leaching involves treating the organic waste with an alkaline solvent such as sodium hydroxide to form sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>). To precipitate the SiO<sub>2</sub>, the Na<sub>2</sub>SiO<sub>3</sub> is neutralized with an acid (Naddaf et al., 2018). Thermal treatment of the extraction of SiO<sub>2</sub> extraction from agricultural wastes involves high temperature in processing of the waste feedstock. This commonly involves the combustion of waste material (Chakraverty et al., 1988; Della et al., 2002; Usman et al., 2014). The aim of this is to increase the relative amount of silicon oxide by reducing the carbonaceous materials present in the sample (Della et al., 2002).

## **2.7 The production of silica by other authors**

Studies of the production of silica from agricultural waste, to be used in different applications has been done by a lot of authors. Kaduku et al. (2015) produced silica from South African coal fly ash for purposes of using it to manufacture sodium silicate, an oil well cement water extender. Kaduku et al. (2015) produced silica by first removing metal oxides such as Al<sub>2</sub>O<sub>3</sub> and CaO by acid refluxing using 3 M HCl at 100 °C for 6 hours. The solid product of silica was then filtered and purified by continuous washing with demineralized water. The SiO<sub>2</sub> was then dried in an oven for 2 hours at 200 °C. An amorphous silica powder was then obtained and analyzed using SEM-EDX, XRD, and Fourier transform infrared spectroscopy.

Setyawan et al. (2019) produced silica from rusk husk by mixing the rusk husk ash with different ratios of NaOH solution. The mixture of the rusk husk ash and the NaOH solution was then heated at 80 °C with constant stirring for 1 hour. This was to dissolve the silica and produce a sodium silicate solution. The solution was then filtered through Whatman no. 41 ash less filter paper. The filtrate was then allowed to cool to room temperature and titrated with 1 N HCL with constant

stirring to pH 7. The silica gel was aged for 24 hours. Distilled water was added to gels and then the gels were broken to make a slurry. The slurries were then washed repeatedly, four times. The gels were then transferred into a beaker and dried at 70 °C for 22 hours to produce xerogels. Some of the silica xerogel samples were crushed and characterized.

Yuvakkumar et al. (2014) produced high purity nano silica powder from rice husk using a simple chemical method. To extract silica from rice husk impurities were first removed by first washing it with it thoroughly with distilled water. The washed rice husk was then air-dried at room temperature and the burned at 973 K for 3 hours in a muffle furnace under an inert temperature. The rice husk ash obtained was also washed with distilled water. This was to remove the sand, light empty grains, dust and fine dirt. Repeated washing of the rice husk ash removed adhered impurities on the silica surface and neutralizes the pH. The neutralized rice husk ash was then refluxed with 6 N HCl for 1.5 hour and then filtered. This was to ensure that pure nano SiO<sub>2</sub> is extracted. The filtered rice husk ash was thoroughly rinse with boiling water and then boiled with various concentration of NaOH solution at 353 K for 1.5 hour, with continuous stirring. The mixture was then filtered to obtain sodium silicate. The obtained residue was continuously washed with hot water for complete extraction of sodium silicate.

Olawale et al. (2019) extracted silica from maize husk by first removing metal impurities by reacting it with acetic acid. The maize husk was then calcinated at a high temperature to produce maize husk ash. To extract silica from maize husk sodium hydroxide pellets of 2 g was first dissolved in 50 mL of water and then stirred until it all dissolved in water. 1 g of maize husk was then added to the NaOH solution. The mixture of NaOH solution and maize husk was then placed in an oven at 100 °C for 1 hour. The precipitate obtained was filtered. The residue was dried for 30 minutes. The obtained product was sodium silicate. 300 mL of 1 N HCl was added to the sodium silicate and kept in an ice water bath for 1 hour. The compound was then filtered and then the residue taken out and dried in an oven for 60 °C. The resultant product obtained was silica in nano scale.

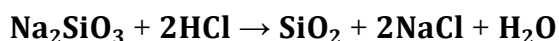
Patil et al. (2014) extracted silica from rice husk by first subjecting rice husk to thermal treatment at a maximum temperature of 700 °C for 6 hours. This was to increase the relative amount of

silicon dioxide by reducing any carbonaceous materials present in the samples. The samples were then cooled down in the furnace. After subjecting rice husk to heat treatment Patil et al. (2014) then extracted silica from rice husk ash by adding 60 mL portions of 1 N NaOH in washed and unwashed rice husk ash. They then boiled the mixture in a covered 250 mL Erlenmeyer flask for 1 hour with constant stirring. This was to dissolve silica and produce sodium silicate solution. The solutions were then filtered through Whatman No. 41 ashless filter paper, and the carbon residues were washed with 100 mL of boiling water. The filtrates and the washings were allowed to cool to room temperature and were titrated at 1 N HCl with constant stirring at pH 7. Silica gel started to precipitate when pH was less than 10. The silica gel formed was aged for 18 hours. The silica was characterized by FTIR and X-ray diffraction (XRD) The resultant silica obtained was amorphous. The silica obtained had small particle size, which made it suitable for use in rubber and ink industries.

Selvakumar et al. (2014) synthesized  $\text{SiO}_2$  through precipitation using different acids namely: hydrochloric acid (HCl), nitric acid ( $\text{HNO}_3$ ) and sulphuric acid ( $\text{H}_2\text{SO}_4$ ), which yielded nano silica. The sample was first treated with acid to remove impurities. NaOH was then added to the washed sample and boiled at constant stirring in a 250 mL covered Erlenmeyer flask to produce  $\text{Na}_2\text{SiO}_3$  solution in the following equation:



The solutions were then filtered and titrated with HCl with constant stirring to pH 7. The silica gel precipitated when the pH was less than 10. The reaction is given by:



Yayha et al. (2017) used citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) to leach, the reason for this is that mineral acids such as; HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  are hazardous to the environment and human and require special disposal treatment which is economically costing. The sample was placed in a 1000 mL beaker which contained  $\text{C}_6\text{H}_8\text{O}_7$  solution. The leaching process was done in

the following conditions: temperature: 30-70 °C, extraction time: 1 hour and citric acid concentration: 2-5%. The tests were done at constant stirring on a magnetic plate. The highest SiO<sub>2</sub> was found at 60 °C and 2% citric acid concentration. Another example of an organic acid that can be used is acetic acid (CH<sub>3</sub>COOH). Acid leaching is not always appropriate as it causes environmental pollution and requires acid resistant equipment; this problem is solved by using alkaline leaching methods (Sahoo et al., 2016).

Sedres (2016) extracted SiO<sub>2</sub> using alkaline leach method. They used NaOH as the alkaline leaching reagent. They used a direct and indirect method of leaching. The direct method which yielded the highest results of SiO<sub>2</sub> uses low temperature. It involves mixing 20g sample with 20 g of NaOH dissolved in 600 mL de-ionized water at a constant temperature of 95 °C at constant stirring for 2 hours. The mixture was then filtered. The filtrates were then diluted to X10, X100 and X1000 dilution. The filtrate was diluted to X10 by adding 10 mL of the filtrate into 100 mL flask and making up the volume using 2% of HNO<sub>3</sub>.

Font et al. (2009) extracted silica from fly ash under the following conditions: Temperature: 50- 150 °C, NaOH solution / fly ash ratio: 2-5 L/Kg, NaOH: 0.5-3 M and extracting times: 1-24 hours. The SiO<sub>2</sub> extraction tests were done with magnetic stirring, using closed heated system in 60 mL Savillex PFA on hot plates for experiments at 50-90 °C. For tests at temperatures greater than 90 °C, a Parr 2L 4843 autoclave reactor was used, with continuous stirring by mechanical agitation, temperature and pressure controls were also

used. This was for a better control and homogeneous application of temperature for experiments at 50-90 °C. The highest SiO<sub>2</sub> was obtained at a 2 M of NaOH in 9 hours.

## **2.8 Optimization of the extraction method using the RMS approach**

Optimization was developed to help develop systems that are cost effective and efficient. They were also developed to develop innovative methods that improve the performance of the existing systems. Optimization in engineering can be classified as a rigorous mathematical approach to identify and select the best candidate from a set of probable design alternatives. Optimization is used to improve business processes in all industries, and it comprises of different techniques such as; computer science, operations research and artificial intelligence. To enhance the creative process of conceptual and detailed design of engineering systems, optimization methods coupled with modern tools of computer-aided design are also utilized (Olawale et al., 2012). Mathematical optimization is a process of minimizing or maximizing an objective function by finding the best available values across a set of inputs.

Using response surface methodology (RSM) approach as a tool in order to assist the extraction of SiO<sub>2</sub> from CFA is considered a very useful model to investigate how several reaction factors influence the extraction over a set of experimental runs. Previous studies on the optimization of extraction dealt with the classical method of experimentation (Matlob et al., 2012). This method involves changing one of the independent extraction parameters while fixing all the remaining parameters at a certain set of conditions (Tayeb et al., 2018). This single-dimensional (factor) search method is extremely time consuming as it involves the need of many experimental runs. It also ignores the interaction between the considered operating parameters which results to a low efficiency in optimization. Statistical methods such as RSM do not only help optimize the extraction method, but they also reduce the total experimental runs, resulting in saving resources and time (Pandey et al., 2016). RSM is a collection of mathematical and statistical techniques used for the purpose of:

- i. Setting up a series of experiments for adequate predictions of a response  $y$ .
- ii. Fitting a hypothesized (empirical) model to data obtained under the chosen design.

- iii. Determining optimum conditions on the model's input (control) variables that lead to minimum or maximum response within a region of interest (Khuri, 2017).

The design of experiments used to establish the RSM model is based on the least of squares method. The diagnostic checking tests specified by the analysis of variance (ANOVA) is used to check the fit of the proposed model. Additionally, a graphical representation plots the surface to locate the optimum and study the surface (Tayeb et al., 2018). As seen in literature, RSM was used to optimize process parameters (Bezerra et al., 2008; Matlob et al., 2012; Olawale et al., 2012; Chitsiga et al., 2018; Ejekwu et al., 2019).

Matlob et al. (2012) used response surface methodology to optimize the extraction of silica from coal fly ash for synthesis of zeolite Na-A. Fifteen experimental conditions for the extraction process were obtained using Box–Behnken design through the manipulation of three independent variables. The variables manipulated were NaOH concentration (2, 4 and 6 M), power level of microwave irradiation (10, 50 and 100 W) and exposure time (1, 3.5 and 6 min). Matlob et al. (2012) found that the optimized conditions of the combined three variables within the experimental range for silica extraction were 5.6 M for NaOH concentration, 5.5 minutes exposure time and 100 W of microwave power level. They also found that NaOH and exposure impacted silica extraction the most than the microwave power level. They also found that the higher NaOH concentration used to extract silica, the higher the silica yield obtained from CFA.

Olawale et al. (2019) used response surface methodology to optimize the production of silica from maize husk. The maize husks were first ground, then washed with acetic acid to remove impurities. The pre-treated maize husk was then subjected to calcination on the experimental runs predicted by Box Behnken Design. The ranges of the variables used were temperature (400 – 700 °C), time (2- 6 h) and the amount of maize husk (5 – 7 g). The above variables were for the pre-treatment of maize husk before the extraction of silica. Olawale et al. (2019) found that the optimal values for the pretreatment of maize husk for the extraction of silica from RMS, namely: temperature, time and the amount of maize husk used were 528 °C, 5.31 hours and 5.85 g. These conditions were validated. The experimental silica yield of 99% agreed closed with the actual silica yield of 99.5%.

## 2.9 The kinetics of the extraction process

Studying the kinetics of a process helps with the determination of whether or not the extraction process is slow or fast. Kinetic study also helps with the understanding of various factors that affect the extraction rate. The extraction is triggered if carried out at optimized conditions stated by the kinetic study. Thus, making the kinetics study to play a vital role in the extraction process. It makes the process economical by saving money, energy and time. Hence, it is important to study the kinetics of system.

Valeev et al. (2018) studied the kinetics of the extraction of iron from coal fly ash by hydrochloric acid leaching. To extract iron, from coal fly ash, hydrochloric acid produced by SIGMATEK LLC was used as a leaching reagent. The leaching of the iron was carried out in a glass flat-bottom flask of 200 mL installed on a heated magnetic stir bar. The experiments were carried out at ambient pressure, 25-100 °C, 5-20% HCl concentration, and over 15-16 min. The amount of ash sample used was 10 g, with a solid-to-liquid ratio of 1 to 10. Upon the completion of the experiment, the pulp slurry was cooled and filtered by vacuum filtration. The solids were then washed with deionized water and dried at 105 °C for 2 hours. The following equation was used to calculate the rate of the Iron and aluminum extraction in solution:

$$\eta = [Me_1 \times V / Me_2] \times 100 \%$$

Where:

$Me_1$  is the content of iron or aluminum in solution after leaching in g/L

$V$  is solution volume after filtration in L

$Me_2$  is the content of iron or aluminum in the feed ash in g/L

Valeev et al. (2018) then plotted four graphs of the extraction efficiency (%) vs Reaction time at the different temperatures (25 – 100 °C) For the effect of temperature, HCl concentration and time of CFA at solution to liquid = 1:10,  $\omega_{stir\ bar} = 300$  rpm: iron extraction efficiency, aluminum extraction efficiency. They expressed the dependence of speed constant of temperature using the Arrhenius Equation:

$$k = A. \exp\left(-\frac{E_a}{RT}\right)$$

Where A is the pre-exponential factor characterizing frequency of reacting molecules collisions;  $E_a$  is the activation energy; and R is the universal gas constant: 8.31 J/K mol.

They then plotted four graphs; two graphs of  $\ln k$  vs  $1/T$  (for iron and aluminum) and two graphs of  $\ln k$  vs  $\ln[\text{HCl}]$  (for iron and aluminum). The slopes of the four graphs gave the activation energy. Diffusion control process generally have low activation energy values (5-20 kJmol<sup>-1</sup>).

The kinetics study showed that the iron leaching process is controlled by chemical reaction and the diffusion process steps. The aluminum leaching process appeared to be controlled by the diffusion process step (Valeev et al., 2018).

## **2.10 Industrial uses of SO<sub>2</sub>**

Silica is used for numerous purposes, such as semi-conductors, high thermal protection fabrics, soda-lime glass, glasses (including lead glass and borosilicate glass) medical devices and contact lenses (Sahoo et al., 2016). There are three ways in which silica is used in the industry, namely as; silica bricks, water extender and glasses.

### **2.10.1 Silica bricks**

Silica bricks contain approximately 95 – 96% SiO<sub>2</sub> and approximately 2% of lime, which is added during grinding to furnish the bond. Their colour varies from white to buff, depending on the type of raw material used. The specific gravity varies from 2.3 – 2.6. These bricks are acid refractories, meaning they are not affected by acids, except for phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and hydrofluoric acid (HF). H<sub>3</sub>PO<sub>4</sub> affect these bricks at a temperature of about 400 C and HF affect these bricks in cold. When silica bricks are heated, their physical strength is much higher than those which are made from clay, which make them more suitable for arches in large furnaces. These bricks have been utilized in co-product coke oven and gas retorts. In general, silica bricks can be used where high resistance to heat is required because they tend to expand on heating (Sharma, 1997).

### 2.10.2 Water extender

Extenders are chemical additives or inert lightweight materials that are used to increase the yield of the cement slurry or decrease the slurry density (Broni-Bediako et al., 2016). The most common water extender is sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) (Saleh Al-Yami et al., 2017).  $\text{Na}_2\text{SiO}_3$  is a clear colorless to light brown solution, made up of water ( $\text{H}_2\text{O}$ ), silicon dioxide ( $\text{SiO}_2$ ) and disodium ( $\text{Na}_2\text{O}$ ). It has varying ratios of  $\text{SiO}_2:\text{Na}_2\text{O}$ ; viscosity and solid contents (Coogee Chemicals, 2018). It is the most commonly used chemical extender for cement slurries. It is said to be five to six times more effective than bentonite on equal concentration basis, because it is available in solid and in liquid form, it is readily adaptable onshore and offshore (Broni-Bediako et al., 2016).  $\text{NaSiO}_3$  is produced through high-temperature calcination (at 1400-1500 °C) of  $\text{SiO}_2$  and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), making the process highly energy intensive resulting to high operational cost (Foletto et al., 2006). In addition, sulphur oxides, nitrogen and dust are emitted during this process which contributes to air pollution. In order to lessen the emission of the above-mentioned waste, the manufacture of  $\text{Na}_2\text{SiO}_3$  through a reaction between  $\text{SiO}_2$  and  $\text{NaOH}$  at high temperature and pressure in an autoclave is preferred (McDaniel, 1961). Water extenders are used in jobs when the hydrostatic head of the cement slurry may surpass the fracture strength of the formation. The reduction of the slurry density results in an increase in the thickening time and a reduction in the ultimate compressive strength (Bett, 2010). Extenders allow more water to be added in the cement slurry, this helps decrease the amount of cement required to produce a given volume for a particular product. Since extenders are cheaper than cement, this brings with a huge amount of saving (Nelson, 1990). A reduction in the slurry density results in the cementing of gas and oil wells in depleted reservoirs or low pressure; the breakdown of weak formation also prevents lost circulation. In addition, the number of stages required to cement a well may be reduced (Shadizadeh et al., 2010). Extenders can be classified as; low density aggregates, gaseous extenders and water extenders, this depends on the mechanism of action. Low density aggregates, is when the density of the materials are lower than the Portland cement, gaseous extenders, is when air or nitrogen ( $\text{N}_2$ ) can be used to form foamed cement in extremely low density and water extenders, is when the presence of water viscosifying agents and clays allow the addition of excess water to achieve the extension of the cement slurry, (Saleh Al-Yami et al., 2017).

### 2.10.3 Glasses

**Fused silica glass** – this type of glass is also known as quartz glass or vitreous silica glass. It used to be made by fusing silica, since it was not obtained in a transparent form it is now made by high temperature pyrolysis of silicon tetrachloride. Properties of fused silica; are high softening point (2600 °F), low specific gravity (2.07), low coefficient of cubical thermal expansion, unusual chemical stability, highest annealing point (1965 °F) and transparency to ultraviolet radiation. As a result of its low thermal expansion, it is used for telescope mirrors (Sharma, 1997).

**High silica glass** – also called Vycor approaches fused silica in some of its properties. It contains about 96%  $\text{SiO}_2$  and 3%  $\text{B}_2\text{O}_3$  and the rest is alkali and alumina. It can also be made from borosilicate glass which when heated separates  $\text{SiO}_2$  as a separate layer. When this layer undergoes hydrochloric (HCl) treatment at a temperature of 98 °C and a second heat treatment it results in a glass containing about 96% glass which is known as high silica glass. Properties of this glass are as follows: highest softening point (2732 °F), highest annealing point which is second after fused silica glass, high chemical durability, stable to all acids except HF, low thermal conductivity, a capacity to resist structural changes during temperature fluctuation, low specific gravity but higher than that of fused silica glass and transparent to almost all ranges of wavelength (Sharma, 1997).

**Borosilicate glass** – This glass contains about 13-28 % of  $\text{B}_2\text{O}_3$  80-87 %  $\text{SiO}_2$ . It is an example of an optical glass. Its properties are as follows: high electrical resistance, low expansion coefficients, superior resistance to shock and chemical resistance. A typical composition of a borosilicate glass is: 80.5%  $\text{SiO}_2$ , 13%  $\text{B}_2\text{O}_3$ , 3%  $\text{Al}_2\text{O}_3$ , 3%  $\text{K}_2\text{O}$  and 0.5%  $\text{Na}_2\text{O}$  (Sharma, 1997).

### 2.11 Concluding remarks

Both coal fly ash and pulp waste contain a percentage of silica. The manufacturing of silica is highly energy intensive, manufactured by smelting quartz at a temperature of 1400 °C (Gandhi et al., 2015). Silica is used in industry to manufacture various silica products such as; silica bricks, silica glasses, water extender ( $\text{Na}_2\text{SiO}_3$ ), etc. (Kaduku et al., 2015). In agricultural waste,  $\text{SiO}_2$  can be extracted using three methods, namely; chemical treatment, thermal treatment, and microbial treatment (Permatasari et al., 2016). Chemical treatment is the most common method of silica extraction in agricultural waste, it involves extraction of silica in agricultural waste by acid leaching or by alkaline leaching. Alkaline leaching is preferred as acid such as; HCl,  $\text{HNO}_3$  and

H<sub>2</sub>SO<sub>4</sub> are hazardous to the environment and human and require special disposal treatment which is economically costing (Yahya et al., 2017). Response surface methodology approach helps optimize the extraction method and it also helps reduce the total experimental runs, resulting in saving resources and time. The extraction study helps with the determination of the SiO<sub>2</sub> extraction rate.

Therefore, in this review, the potential of extracting SiO<sub>2</sub> from the PW and CFA, SiO<sub>2</sub> extraction optimization of the SiO<sub>2</sub> and the purpose of performing a kinetic study was investigated. The next chapter discusses materials and analytical methods used in this study.

## **Chapter 3: Methodology**

### **3.1 Introduction**

Relevant literature has been explored and reviewed hence the birth of this chapter to lay down the methodology for this work. This chapter details the analytical, experimental equipment and the techniques used for the extraction of silica from coal fly ash (CFA) and pulp waste ash (PWA). The optimization of the extraction of SiO<sub>2</sub> from CFA and the kinetic study of the SiO<sub>2</sub> extraction from the two waste materials. This study has been divided into the following steps as shown in Figure 3-1.

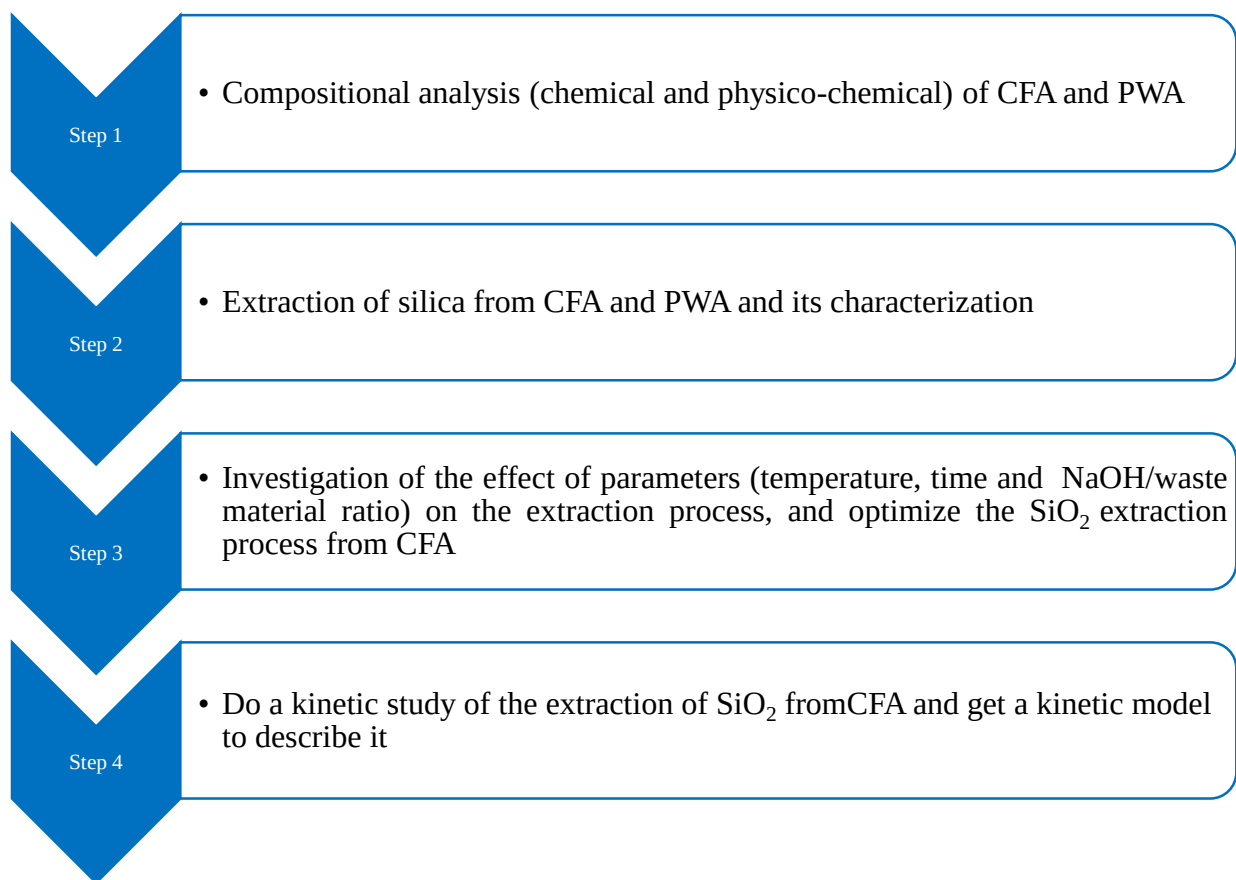


Figure 3-1 Overview of the methodology employed in this study

### 3.2 Chemical and chemical reagents

Chemicals and chemical reagents used for the various experiments were analytical reagent grade and were used without further purification. Sodium hydroxide pellets and hydrochloric acid were purchased from Sigma-Aldrich (Pvt) Ltd, Republic of South Africa. Deionized water was used for all the experiments that were performed in aqueous media.

### 3.3 Sampling

South African coal fly ash was collected from Matla Power Station, in Mpumalanga province in the Republic of South Africa. Pulp waste (PW), a by-product of the manufacturing of paper was supplied by the Universal Paper Manufactures in South Africa. PW was calcinated at 650 °C for 2 hrs to form pulp waste ash. The samples of coal fly ash, pulp waste and pulp waste ash are shown in Figure 3-2.



Figure 3-2 As received (A) South African coal fly ash (B) pulp waste (C) pulp waste ash

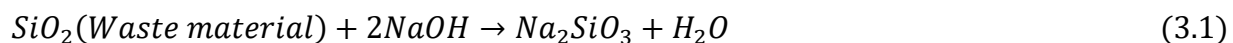
### 3.3.1 Comprehensive characterization of coal fly ash and pulp waste ash

Thermal behavior of CFA and PWA was investigated by using a thermogravimetric analyzer (TGA) (Q600 SDT Thermal Analyzer TA Instrument, USA). The samples were heated in the absence of oxygen at a rate of 10 °C/min to a temperature of 800 °C. Chemical analysis of the two wastes materials was carried out via X-Ray Fluorescence Spectrophotometer (Panalytical PW2404 X-ray Fluorescence Spectrophotometer). A Field Emission Scanning Electron Microscope (Carl Zeiss Sigma FESEM Oxford XACT EDX detector) equipped with Energy-dispersive X-ray was used to check morphology and elemental composition. The results and findings are discussed in Chapter 4.

### 3.4 Extraction of SiO<sub>2</sub> from CFA and PWA

SiO<sub>2</sub> was synthesized from CFA and PWA by adapting the method reported by Olawale et al. (2019)

CFA and PWA were each mixed with 2 M of NaOH solution at a NaOH solution/waste ratio of 3.5 mL/g and boiled for 45 min at a temperature of 70 °C, with constant stirring at an agitation speed of 250 rpm, to produce sodium silicate (Na<sub>2</sub>SiO<sub>2</sub>) solution, shown in Eq. 3.1.



The solution was then filtered, and the filtrate allowed to cool to room temperature. To precipitate SiO<sub>2</sub>, the filtrate was then titrated until pH 5.0 (this was to ensure that all the SiO<sub>2</sub> have completely precipitates) with 3M HCl solution (music et al., 2011). The solution with the precipitated SiO<sub>2</sub> was then filtered and dried in an oven at a temperature of 110 °C for 2 hrs. The equation for the reaction of Na<sub>2</sub>SiO<sub>2</sub> and HCl to produce SiO<sub>2</sub> is shown in Eq. 3.2.



The dried  $\text{SiO}_2$  powder produced from CFA and PWA was weighed to calculate the % yield using the equation shown in Eq. 3.3 (Rovani et al., 2019).

Silica extraction yield:

$$= \frac{\text{mass of SiO}_2 \text{ produced}}{\text{mass of waste material utilized} \times \% \text{ of SiO}_2 \text{ in the waste material}} \times 100 \quad (3.3)$$

The  $\text{SiO}_2$  obtained from the two waste materials was then analyzed using TGA and SEM. Experimental procedures of the extraction of silica from CFA and PWA is shown in Figure 3-3.

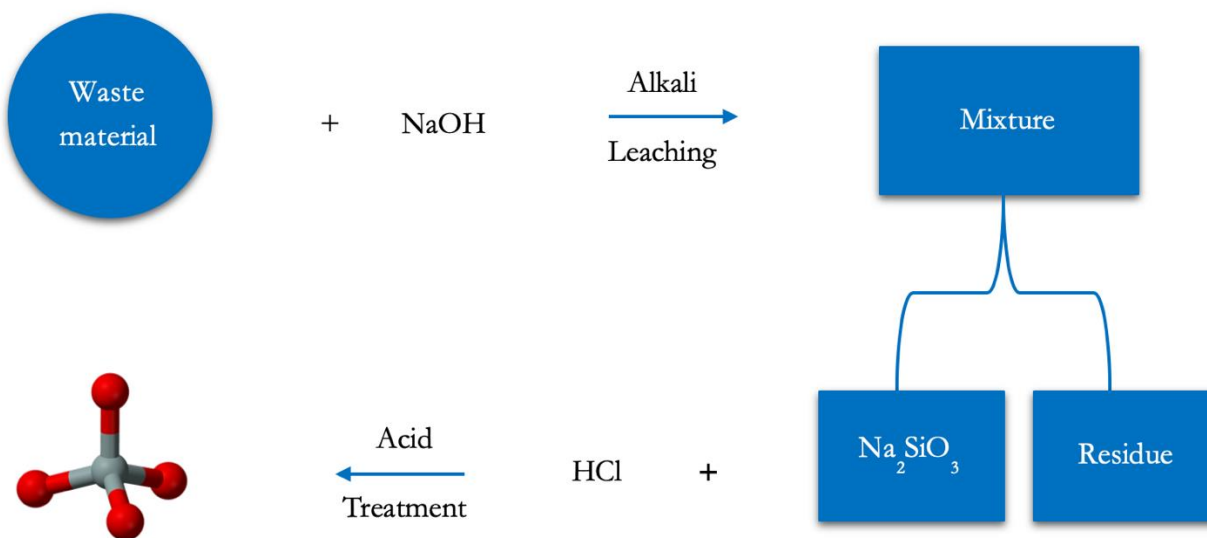


Figure 3-3 Steps of experimentation for the extraction of  $\text{SiO}_2$  from CFA and PWA

### 3.5 Instrumental Characterization of Silica

To study the properties of the extracted silica thermogravimetric analysis (TGA) and Scanning Electron Microscopy (SEM) was used.

### 3.5.1 Thermogravimetric analysis

Thermal behavior of the extracted silica was investigated by using a thermogravimetric analyzer (TGA) (Q600 SDT Thermal Analyzer TA Instrument, USA). The samples were heated in the absence of oxygen at a rate of 10 °C/min to a temperature of 800 °C.

### 3.5.2 Scanning electron microscopy

Scanning electron microscopy makes it possible to observe the morphology of the samples. The samples were double coated with 60% palladium and 40% gold (Pd/Au) prior to SEM analysis to prevent charge build-up. A Field Emission Scanning Electron Microscope (Carl Zeiss Sigma FESEM Oxford XACT EDX detector) equipped with Energy-dispersive X-ray was used to check morphology and elemental composition of the silica extracted from the two waste materials.

## 3.6 Design of Experiments (DoE)

The experimental design is shown in Table 3-1, the experimental data was analyzed using RSM to fit the second order polynomial equation created by Design-Expert 7 software (Stat-Ease Inc., USA). The parameters that were selected for this study are as follows: Time (30 – 60 min), temperature (50 – 90 °C), NaOH concentration (1 – 3 M) and NaOH solution/waste ratio (2 – 5 mL/g). Central composite design (CCD) which consisted of a total of 30 experiments was used in this study (16 factorial points, 6 center points and 8 axial points) to optimize the SiO<sub>2</sub> yield extracted from coal fly ash. The 30 experiments are shown in Table 3-2. The preliminary studies conducted gave the central point (Temperature of 70 °C, NaOH concentration of 2 M, NaOH solution to waste ratio of 3.5 mL/g and an extraction time of 45 min). CCD was adopted in this study because a smaller number of experiments is required compared to the traditional method which requires one variable to be varied at a time, this is time consuming and expensive (Chitsiga et al., 2018). Another disadvantage of the one-variable-at-a-time is that, it does not take into account the interactive effect between the parameters being investigated. As a result, it does not show the complete effect of the parameters on the response (Bezerra et al, 2008).

Table 3-1 Experimental variables at different levels used for the production of SiO<sub>2</sub> from CFA using CCD

| Variables | Units | Symbol | Levels |
|-----------|-------|--------|--------|
|-----------|-------|--------|--------|

|                              |      |   | -1 | 0   | 1  |
|------------------------------|------|---|----|-----|----|
| Temperature                  | °C   | A | 50 | 70  | 90 |
| NaOH Concentration           | M    | B | 1  | 2   | 3  |
| NaOH Solution to Waste Ratio | mL/g | C | 2  | 3.5 | 5  |
| Extraction Time              | min  | D | 30 | 45  | 60 |

The upper and lower limits considered in this study were adapted Font et al. (2009).

Table 3-2 Experimental runs from the CCD

| Run | Variable               |                              |                                         |                             |
|-----|------------------------|------------------------------|-----------------------------------------|-----------------------------|
|     | A: Temperature<br>(°C) | B: NaOH<br>Concentration (M) | C: NaOH Solution:<br>Waste Ratio (mL/g) | D: Extraction<br>Time (min) |
| 1   | 50                     | 1                            | 5                                       | 30                          |
| 2   | 70                     | 2                            | 3.5                                     | 45                          |
| 3   | 70                     | 4                            | 3.5                                     | 45                          |
| 4   | 50                     | 1                            | 5                                       | 60                          |
| 5   | 70                     | 2                            | 3.5                                     | 45                          |
| 6   | 70                     | 2                            | 3.5                                     | 75                          |
| 7   | 90                     | 3                            | 2                                       | 30                          |
| 8   | 70                     | 2                            | 3.5                                     | 45                          |
| 9   | 70                     | 2                            | 0.5                                     | 45                          |
| 10  | 50                     | 3                            | 2                                       | 30                          |
| 11  | 70                     | 0                            | 3.5                                     | 45                          |
| 12  | 70                     | 2                            | 3.5                                     | 45                          |
| 13  | 90                     | 3                            | 5                                       | 30                          |

|    |     |   |     |    |
|----|-----|---|-----|----|
| 14 | 70  | 2 | 6.5 | 45 |
| 15 | 110 | 2 | 3.5 | 45 |
| 16 | 70  | 2 | 3.5 | 45 |
| 17 | 50  | 3 | 2   | 60 |
| 18 | 50  | 1 | 2   | 60 |
| 19 | 50  | 1 | 2   | 30 |
| 20 | 30  | 2 | 3.5 | 45 |
| 21 | 90  | 1 | 5   | 60 |
| 22 | 90  | 1 | 5   | 30 |
| 23 | 70  | 2 | 3.5 | 15 |
| 24 | 90  | 3 | 2   | 60 |
| 25 | 90  | 3 | 5   | 60 |
| 26 | 90  | 1 | 2   | 30 |
| 27 | 50  | 3 | 5   | 30 |
| 28 | 90  | 1 | 2   | 60 |
| 29 | 70  | 2 | 3.5 | 45 |
| 30 | 50  | 3 | 5   | 60 |

The set of experiments presented in Table 3-2 were performed by using the method shown in Figure 3-3. The experiment was conducted by varying the parameters shown in Table 3-1.

### 3.7 Model formulation and statistical analysis

A quadratic model having % silica yield ( $Y$ ) from CFA was developed using the experimental data obtained from Section 3.6. The general regression model for a quadratic (Eq. 3.4) model was adopted.

$$Y = \alpha_0 + \alpha_1 A + \alpha_2 B + \alpha_3 C + \alpha_4 D + \alpha_{12} AB + \alpha_{13} AC + \alpha_{14} AD + \alpha_{23} BC + \alpha_{24} BD + \alpha_{34} CD + \alpha_{11} A^2 + \alpha_{22} B^2 + \alpha_{33} C^2 + \alpha_{44} D^2 + \epsilon \quad (3.4)$$

In the above equation, A, B, C and D represent the independent variables symbols temperature, NaOH concentration, NaOH solution to waste ratio and extraction time, respectively. The coefficients for the linear terms in the two expressions are represented by  $\alpha_0, \alpha_1, \alpha_2, \alpha_3$  and  $\alpha_4$  and the coefficients for the quadratic terms are represented by  $\alpha_{11}, \alpha_{22}, \alpha_{33}$  and  $\alpha_{44}$ . To determine the statistical significance of the model analysis of variance (ANOVA) test was conducted on the

model. Additionally, parametric effect of the investigated variables on the extraction of  $\text{SiO}_2$  from CFA was studied by obtaining response surfaces and contours from the model.

### **3.8 Desirability function**

To optimize the operating conditions of extraction of  $\text{SiO}_2$  from CFA, numerical optimization by desirability function was used. This technique can be used to determine the optimum conditions of one or more responses. To optimize the overall desirability of the outcome, the independent variable levels together produce the most desirable outcomes for the response is first determined. The overall desirability outcome is then maximized based on the factors which can be controlled (Ejekwu et al., 2019). In numerical optimization, to maximize the response (silica yield) in CFA, the desired goal for each factor was chosen. The goal for all the factors were set to be within range and the silica yield, maximum.

### **3.9 Kinetic study**

To determine whether or not the extraction of silica from CFA can be explained using a kinetic model, a kinetic study was done. The experiments for the kinetic study of the extraction of silica from CFA were carried out as follows:

The reactions were carried out in a 250 mL Erlenmeyer flask at temperatures 50 °C, 60 °C, 70 °C, 80 °C at a solution to waste ratio of 5 mL/g (50 g of waste was added to 250 mL of NaOH solution) at an agitation speed of 250 rpm. The reaction mixtures were run for 30, 40, 50, 60 minutes for each temperature. Once the reaction was stopped, the  $\text{Na}_2\text{SiO}_2$  solution produced as shown in Eq. 3.1. The solutions were then filtered, and the filtrates allowed to cool to room temperature. To precipitate  $\text{SiO}_2$ , the filtrates were then titrated until pH 5.0 with 3 M HCl solution. The solution with the precipitated  $\text{SiO}_2$  was then filtered and dried in an oven at a temperature of 110 °C for 2 hrs. The equation for the reaction of  $\text{Na}_2\text{SiO}_2$  and HCl to produce  $\text{SiO}_2$  is shown in Eq. 3.2. The dried  $\text{SiO}_2$  powder produced from CFA was weighed to calculate the % yield using the equation shown in Eq. 3.3

### 3.9.1 Determination of kinetics

The interaction between CFA (A) and NaOH (B) to give SiO<sub>2</sub> (C) is given by the stoichiometric relationship in Eq. 3.6:



The extraction rate of component was assumed as a function of SiO<sub>2</sub> recovery from Eq. 3.3 as follows:

$$-\frac{dA}{dt} = k \cdot A \quad (3.7)$$

Where  $\frac{dA}{dt}$  = SiO<sub>2</sub> extraction rate  $k$  = *chemical* reaction rate constant;  $A$  = residual SiO<sub>2</sub>

To determine the kinetic reaction constant ( $k$ ), a linear regression curve was created based on the equation below and  $k$  was determined based on the slope of the line.

$$\ln[A] = -kt + \ln[A]_0 \quad (3.8)$$

Where  $A$  is the total SiO<sub>2</sub> at time  $t$ ;  $A_0$  = total SiO<sub>2</sub> at  $t = 0$ .

The rate constants at different temperatures were then fitted to the Arrhenius equation. Where the slope and the intercept of the plots represent the ( $E_a/R$ ) and  $\ln A$  in Eq. 3.8, respectively. The Arrhenius equation is:

$$k = Ae^{-\frac{E_a}{RT}} \quad (3.9)$$

By taking the natural log for both sides of Eq. 3.9, Eq. 3.10 was obtained.

$$\ln k = \frac{E_a}{RT} + \ln A \quad (3.10)$$

Where;

- $k$  represents the rate constant of reaction in  $\text{min}^{-1}$
- $A$  represents the pre-exponential factor in  $\text{min}^{-1}$
- $E_a$  is activation energy in  $\text{J.mol}^{-1}$
- $R$  is gas constant,  $8.314 \text{ J.mol}^{-1} \cdot \text{K}^{-1}$
- $T$  is temperature in K

Eqs. 3.6 – 3.10, were adapted from Ejekwu et al. (2019).

### 3.9.10 Concluding remarks

In this chapter, A short overview of the methods used in the characterization of the coal fly ash, pulp waste ash and silica extracted from the two wastes materials is presented. This chapter also provides a short overview of the methods used to extraction silica, optimization the silica extraction from coal fly ash and to perform a kinetic study of the extraction of silica from coal fly ash. Results obtained from the experimental procedures described in this chapter are reported and discussed in subsequent chapters.

## **Chapter 4: Physico-Chemical Properties of CFA and PWA**

### **4.1 Introduction**

In this chapter, results of the physico-chemical properties of coal fly ash (CFA) and pulp waste ash (PWA) are reported.

### **4.2 Experimental**

The detailed method applied in the physico-chemical properties study of CFA and PWA is detailed in Chapter 3 (Section 3.3.1).

### **4.3 Results and Discussion**

#### **4.3.1 XRF analysis**

The XRF results showed that both CFA and PWA are sources of  $\text{SiO}_2$ , they also showed that CFA has a higher  $\text{SiO}_2$  composition compared to PWA, consisting of 57.9% and 33.04%, respectively. The analysis showed that the major components of CFA and PWA are silica, alumina and calcium oxide. For CFA the order of the metal oxides decreases in the order  $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{CaO} > \text{TiO}_2 > \text{MgO} > \text{K}_2\text{O} > \text{P}_2\text{O}_5 > \text{Fe}_2\text{O}_3 > \text{Na}_2\text{O} > \text{MnO}$  (see Table 4-1 and Table 4-1). This order is consistent with the previous reports of South African CFA (Ayanda et al., 2012; Mainganye et al., 2013; Ikotun et al., 2014; Kaduku et al., 2015). For PWA the metal oxides decrease in the order  $\text{Al}_2\text{O}_3 > \text{SiO}_2 > \text{CaO} > \text{Na}_2\text{O} > \text{MgO} > \text{K}_2\text{O} > \text{TiO}_2 > \text{Fe}_2\text{O}_3 > \text{P}_2\text{O}_5 > \text{MnO} > \text{Cr}_2\text{O}_3 > \text{NiO}$ . The XRF for CFA correspond to the one reported in literature obtained by Kaduku et al. (2015) shown in Table 4-1. They also obtained  $\text{SiO}_2$  composition of 57.9%,  $\text{Al}_2\text{O}_3$  to be 31.12% and  $\text{Fe}_2\text{O}_3$  to be 33% (see Table 4-1). The composition of silica is lower than that of alumina in PWA unlike in literature where; Abdullahi (2006), Naik et al. (2003) and Vassilev et al. (2013) found the composition of silica to be comparatively higher than that of alumina (Table 4-2).

Table 4-1 XRF results of CFA compared with literature

| Chemical Oxide Formula |                         | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MnO  | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | NiO  | LOI  |
|------------------------|-------------------------|------------------|--------------------------------|--------------------------------|------|------|------|-------------------|------------------|------------------|-------------------------------|-----------------|--------------------------------|------|------|
| % Composition          | CFA                     | 57.90            | 31.12                          | 0.33                           | 0.04 | 0.95 | 4.28 | 0.13              | 0.66             | 1.52             | 0.39                          | N/P             | 0.02                           | 0.00 | 0.73 |
|                        | Kaduku et al. (2015)    | 57.90            | 31.12                          | 0.33                           | 0.04 | 0.95 | 4.28 | 0.13              | 0.66             | 1.52             | 0.39                          | N/P             | 0.02                           | 0.00 | 0.73 |
|                        | Mainganye et al. (2013) | 55.66            | 27.95                          | 3.22                           | 0.04 | 1.91 | 4.38 | 0.13              | 0.48             | 1.13             | 0.26                          | N/P             | 0.03                           | N/P  | 4.74 |
|                        | Ayanda et al. (2012)    | 51.43            | 30.93                          | 2.29                           | 0.02 | 1.95 | 6.75 | 0.54              | 0.77             | 1.74             | 1.08                          | N/P             | 0.02                           | 0.01 | 1.21 |

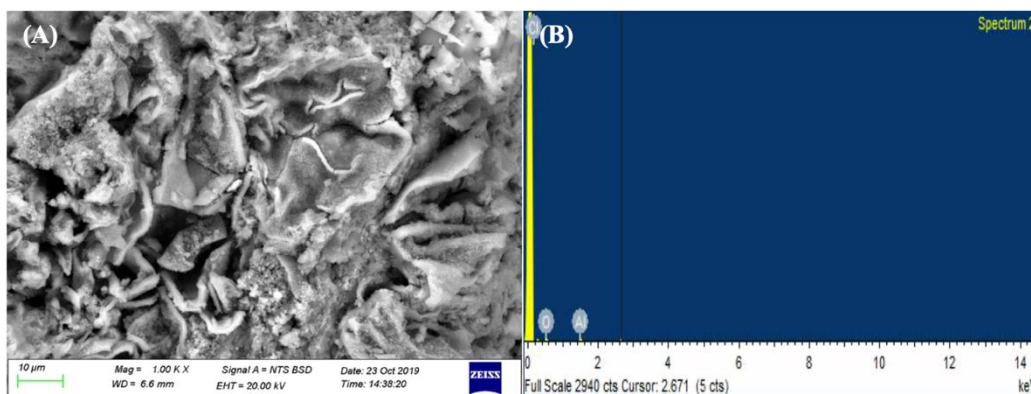
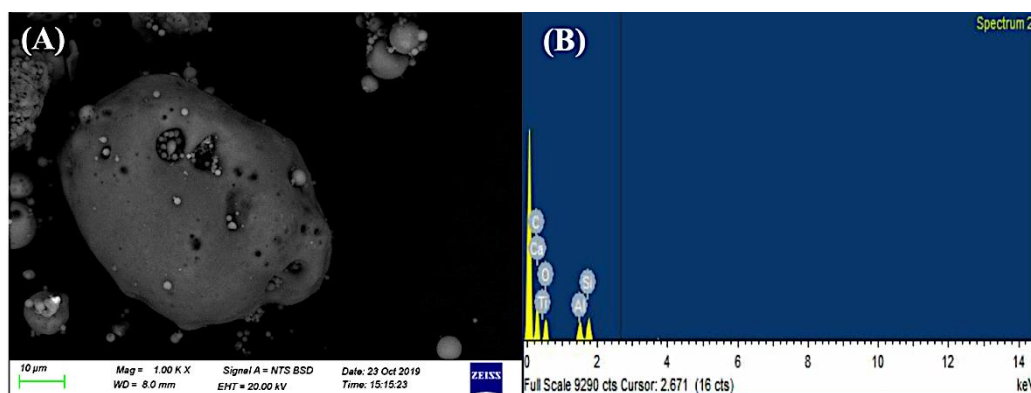
Table 4-2 XRF results of PWA compared with literature

| Chemical Oxide Formula |                        | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MnO  | MgO  | CaO   | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | NiO  | LOI   |
|------------------------|------------------------|------------------|--------------------------------|--------------------------------|------|------|-------|-------------------|------------------|------------------|-------------------------------|-----------------|--------------------------------|------|-------|
| % Composition          | PWA                    | 33.04            | 39.76                          | 0.82                           | 0.04 | 1.10 | 11.55 | 1.43              | 1.08             | 0.98             | 0.50                          | N/P             | 0.03                           | 0.00 | 10.00 |
|                        | Naik et al. (2003)     | 26.50            | 9.00                           | 5.40                           | N/P  | 3.00 | 16.00 | 1.7               | 5.00             | 0.51             | N/P                           | N/P             | N/P                            | N/P  | N/P   |
|                        | Vassilev et al. (2013) | 31.60            | 13.2                           | 5.12                           | 2.77 | 5.40 | 28.90 | 1.42              | 13.20            | N/P              | 2.64                          | 2.67            | N/P                            | N/P  | N/P   |
|                        | Abdullahi (2006)       | 31.80            | 28.00                          | 2.34                           | N/P  | 9.32 | 10.53 | 6.50              | 10.38            | N/P              | N/P                           | N/P             | N/P                            | N/P  | N/P   |

#### 4.3.2 FESEM-EDX analysis

The FE-SEM images and EDS spectrum of CFA and PWA observed by Field Emission Scanning Electron Microscope and Energy Dispersive X-ray analysis are shown in Figure 4-1 and Figure 4-2, respectively. The particles of CFA (Figure 4-1) are predominantly spherical in shape with a relatively smooth surface and a wide particle size range. This was also observed in literature by other authors (Ayanda et al., 2012; Mainganye et al., 2013; Kaduku et al., 2015). The smoothness of the particle may be due to the fact that these particles are covered in amorphous glass phase. The spherical shape of fly ash particles is formed as a result of relatively sudden cooling during combustion process. The spherical particles are either opaque or non-opaque spheres (Mainganye et al., 2013). The Opaque spheres are mostly iron oxides and some silicates whilst the non-opaque spheres mostly silicates (Fisher et al., 1978). Figure 4-1 also indicates that the small spherical particles, consisting of hollow spheres (cenospheres) and some spheres containing other spheres

(plerospheres), are attached to the larger particles (Mainganye et al., 2013). The FE-SEM image also indicates the presence of non-spherical particles, this is due to the incomplete combustion of coal components that occurred as a result of less exposure to high temperature (Fisher et al., 1978). The EDS spectrum of CFA (Figure 4-1) revealed the presence of C, Ca, O, Ti, Al and Si. The FE-SEM image of PWA (Figure 4-2) shows pulp waste ash as a heterogeneous mixture of particles in varying sizes. The particles are irregular and angular shaped inorganic particles with thin layers of crystalline structures. The irregular particles are hydrophilic in nature and absorb waters into their pores through capillary action simultaneous to the hydration oxides. Some particles have a porous cellular form: they are the result remains of unburned or partially wood chips, knots or bark particles (Cherian & Siddiqua, 2019). A similar morphology for pulp waste ash was also observed by other authors in literature (Cherian & Siddiqua, 2019; Grau et al., 2015, Naik & Kraus, 2003; Olanders & Steenari, 1995). The EDS spectrum of PWA (Figure 4-3) reveals the presence of Cl, O and Al.



### 4.3.3 Thermogravimetric analysis

The results for thermogravimetric analysis for CFA and PWA are shown in Figure 4-3. Thermogravimetric analysis makes it possible to follow the weight loss of samples as function of temperature. The TGA plot of CFA showed the weight loss at a temperature of 20 °C while the PWA curve showed weight loss at 23 °C. A total weight loss of 1 wt % was observed for CFA within 20 °C and 890 °C temperature range, while a total weight loss of 33 wt% was observed for PWA. Between room temperature and 100 °C a weight loss of 0.05 wt% is indicated for CFA and 1.6 wt% for PWA, this indicates loss of humidity (Mohomane et al., 2017). The weight loss which is a result of decomposition of volatile matter is shown between 100 °C and 340 °C CFA (0.1 wt%), while PWA (8 wt%) is indicated between 100 and 230 °C. The loss of mass, due to the decomposition of  $\text{CaCO}_3$  for CFA (0.5 wt%) is shown between 500 °C and 890°C while for PWA (15 wt%) is shown between 273 °C and 992 °C. The small weight loss of the two waste materials is due to the high ash content (dos Santos et al., 2014). The investigation of the thermal events of the two waste materials is important as the extraction of  $\text{SiO}_2$  involves heat application.

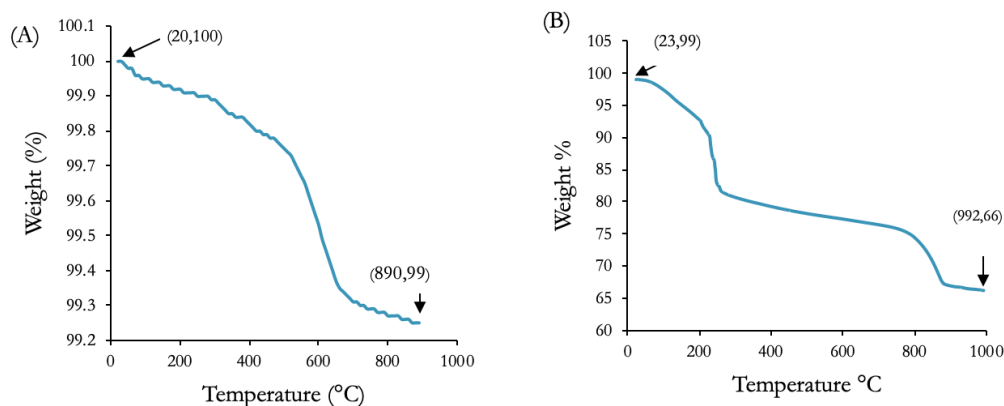


Figure 4-3 Thermogravimetric weight loss (%) vs. Temperature (°C) curves for (A) CFA and (B) PWA

### 4.4 Concluding remarks

The compositional analysis study of coal fly ash and pulp waste ash confirms that silica is the predominant compound in the samples. The XRF results revealed that the coal fly ash and pulp waste ash contained 57.90% and 33.04% of silica, respectively. The extraction of silica from coal fly ash and pulp waste ash is therefor worth pursuing as both waste materials contain silica.

## **Chapter 5: The Extraction of Silica from Coal Fly Ash and Pulp Waste Ash**

### **5.1 Introduction**

This chapter discusses the results obtained for the extraction of Silica from coal fly ash and pulp waste ash.

### **5.2 Experimental**

To extract silica from coal fly ash and pulp waste ash, the two waste materials were each mixed with 2 M of NaOH solution at a solution/waste ratio of 3.5mL/g and boiled for 45 min at a temperature of 70 °C. With constant stirring at an agitation speed of 250 rpm, to produce sodium silicate ( $\text{Na}_2\text{SiO}_2$ ) solution. The solution was then filtered through Whatman No. 41 ashless filter paper, and the filtrate allowed to cool to room temperature. To precipitate  $\text{SiO}_2$ , the filtrate was then titrated until pH 5.0 with 3M HCl solution. The solution with the precipitated  $\text{SiO}_2$  was then filtered and dried in an oven at a temperature of 110 °C for 2 hrs. The dried  $\text{SiO}_2$  powder produced from CFA and PWA was weighed to calculate the %yield using the Equation 3.3 in Chapter 3. The extracted silica was then characterized using SEM and TGA. The comprehensive characterization methods applied to CFA and PWA are described in detail in Chapter 3 (Section 3.5) of this thesis.

### **5.3 Results and discussion**

#### **5.3.1 The amount of silica extracted from coal fly ash and pulp waste ash**

10.98% and 37.59% of silica was extracted from coal fly ash and pulp waste ash, respectively. A higher yield was extracted from pulp waste ash than from coal waste ash. The low  $\text{SiO}_2$  yield extracted from the two waste materials could be as a result of the 2 M concentration of NaOH that was used to extract  $\text{SiO}_2$  in both waste materials, which is not enough to extract a high yield of  $\text{SiO}_2$ . According to Matlob et al. (2012),  $\text{SiO}_2$  yield was low at NaOH from 2–3.5 M, while a higher yield was obtained from 4.5-6 M of NaOH.

### 5.3.2 FESEM-EDX analysis of the extracted silica

Figure 5-1 shows the FE-SEM images of the amorphous  $\text{SiO}_2$  extracted from CFA and PWA. The images are all similar to that of the  $\text{SiO}_2$  extracted by Music et al. (2011) and Kaduku et al. (2015). Figure 5-2 shows the EDS spectrum of the amorphous  $\text{SiO}_2$  extracted from CFA and PWA. The two spectrums showed the presence of silicon and oxygen, confirming this is indeed  $\text{SiO}_2$  which was precipitated from the two waste materials. The EDS spectrum also showed the presence of sodium, chloride and aluminum ions, this indicates that the ions were not well removed in their mother liquor (Music et al., 2011). The presence of the low amount of carbon could be from CFA and PWA (Adam et al., 2011).

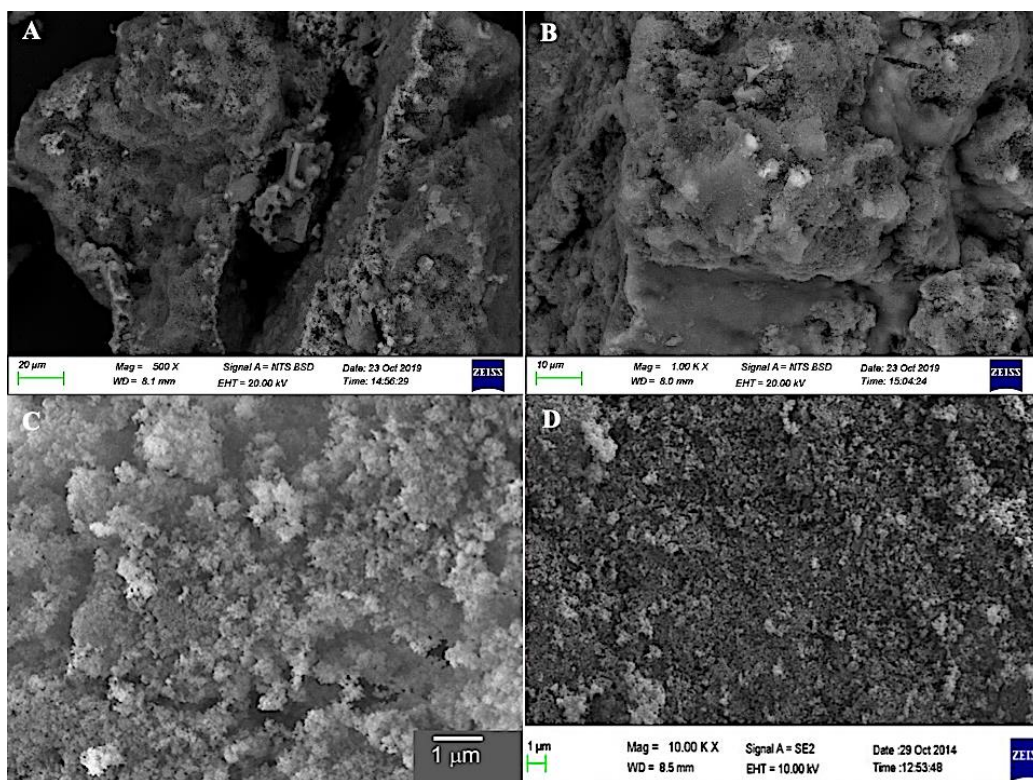


Figure 5-1 Morphology of extracted  $\text{SiO}_2$  from (A) CFA, (B) PWA, from literature (C) and (D)

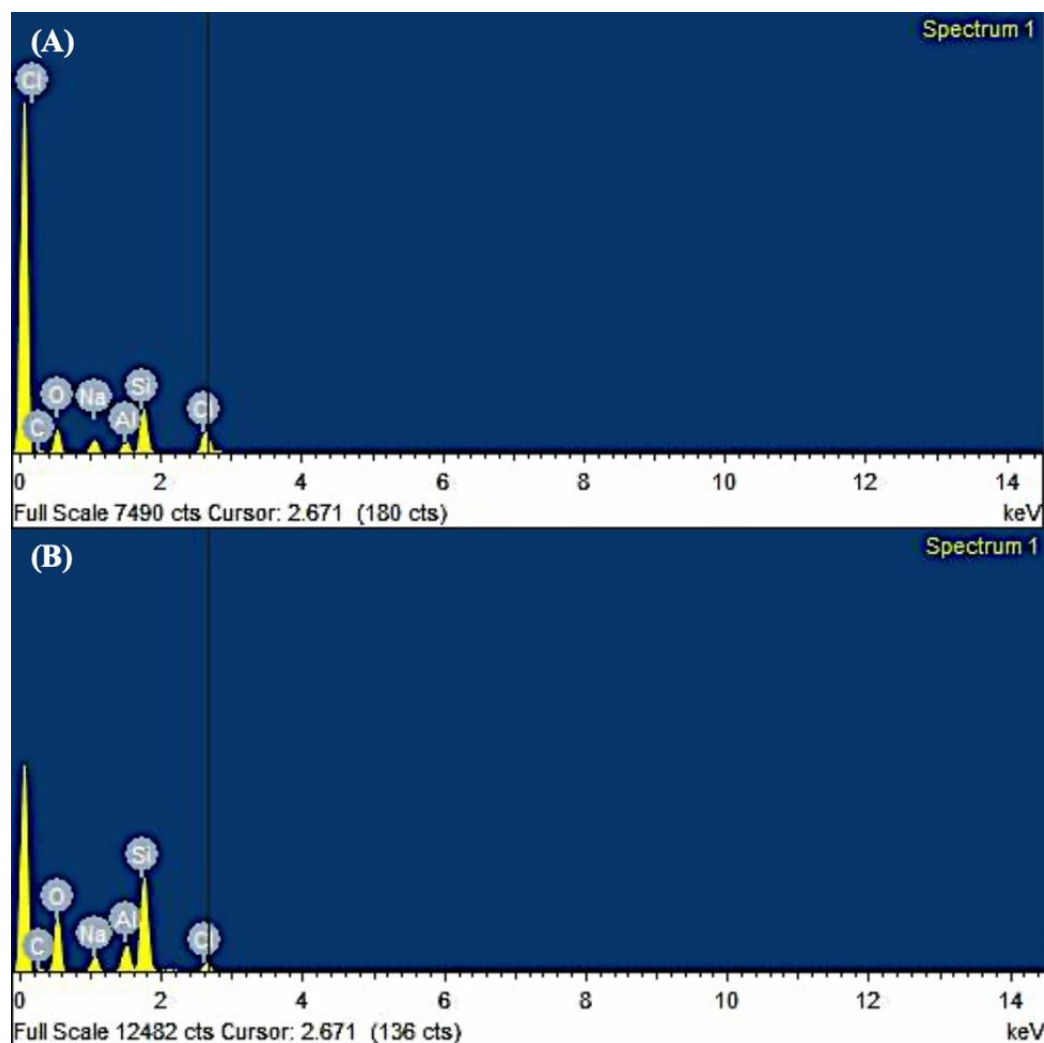


Figure 5-2 EDS spectrum of extracted SiO<sub>2</sub> from CFA (A) and PWA (B)

### 5.3.3 Thermogravimetric analysis results

The TGA weight loss curves for the SiO<sub>2</sub> extracted from CFA and PWA are shown in Figure 5-3. A weight loss at just above 20 °C is observed for the SiO<sub>2</sub> extracted from both waste materials. This is due to the evaporation of physically adsorbed water molecules (Lin and Zhou, 2017). This low temperature weight loss is also similar to the commercial SiO<sub>2</sub> reported in literature (Lin and Zhou, 2017; Ivan et al. 2003). The weight loss of the extracted SiO<sub>2</sub> from CFA is significantly higher than that of commercial SiO<sub>2</sub> by 5 wt% (Lin and Zhou, 2017). A total weight loss of about 30 wt% is observed from SiO<sub>2</sub> extracted from CFA while a total weight loss of 60 wt% is observed in silica extracted from PWA. This means SiO<sub>2</sub> extracted from CFA is lightly more thermally stable than that extracted from PWA. The above results indicate that the SiO<sub>2</sub> extracted from the

two wastes materials are thermally stable only at lower temperatures and can be used up to 20 °C only (Arora et al., 2018).

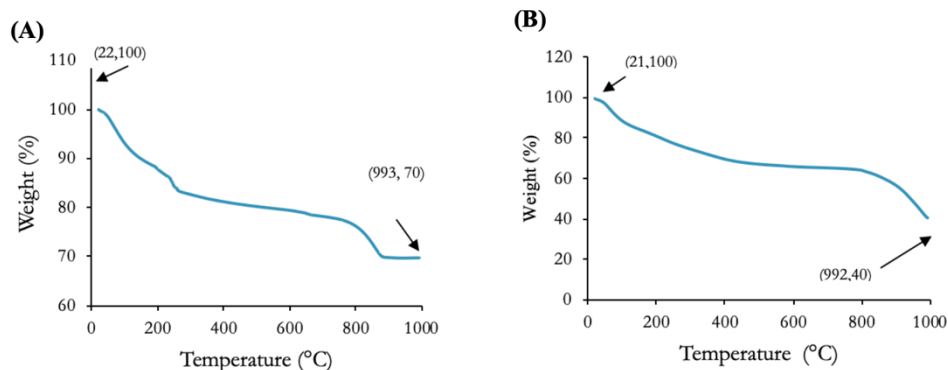


Figure 5-3 TGA weight loss (%) vs Temperature (°C) curves of the SiO<sub>2</sub> extracted from (A) CFA, (B) PWA

#### 5.4 Concluding remarks

SiO<sub>2</sub> was successfully extracted from CFA and PWA. A higher yield of 37.59% SiO<sub>2</sub> was extracted from PWA than from CFA (10.96%). The FE-SEM images of the silica extracted from CFA and PWA are similar to the silica extracted in literature. The EDS spectrums of the silica extracted from the two wastes materials showed the presence of silicon and oxygen indicating that the material extracted was indeed silica. The TGA weight loss curves of the extracted silica was found to be the similar to the one in literature. Therefore, the results in this chapter showed that SiO<sub>2</sub> was successfully extracted from CFA and PWA through alkaline leaching. It also showed that at the same extraction conditions, a higher SiO<sub>2</sub> yield is extracted from PWA.

## Chapter 6: Optimization of Silica Extraction

### 6.1 Introduction

Designing products and systems requires a deep understanding of influences that achieve a desirable performance. The need for efficient and systematic decision-making approach drives the need for optimization strategies (Biegler, 2010).

Optimization in engineering is defined as a rigorous mathematical approach to identify and select the best candidates from a set of probable design alternatives (Olawale et al., 2012). In process engineering, the main objective of optimization is to maximize the yield, minimize variability and improve the process (Shermi, 2013).

There are three times of optimization, namely; topological optimization, operating-procedure optimization and parametric optimization. Topological optimization is concerned with using equipment to its fullest advantage (Simate et al, 2009). Operating-procedure optimization is concerned with instructions detailing relevant steps to accomplishing tasks or activities of process in the best way possible (Edgar and Himmelblau, 1988). Parametric optimization is concerned with operating variables such as pressure, temperature, pH, agitation speed and solution to solid ratio for a given process (Shermi, 2013).

In this study, parametric optimization was deemed fit using a statistically based optimization approach, response surface methodology (RSM) to determine the optimum conditions of temperature, NaOH concentration, NaOH solution to waste ratio and extraction time for the extraction of SiO<sub>2</sub> from CFA. RSM is a collection of tools developed in the 1950s for the purpose of determining optimum operating condition in the chemical industry (Meyers et al., 1989)

This chapter discusses the results obtained for the effect of the operating variables on the extraction of SiO<sub>2</sub> from CFA, as well as the optimization results, using response surface methodology (RSM) approach.

## **6.2 Experimental**

The detailed method applied to study the effect of the operating variables on the extraction of silica from CFA, as well as the optimization of the extraction conditions of silica is described in detail in Chapter 3 (Sections 3.6 – 3.8) of this thesis.

## **6.3 Results and discussion**

### **6.3.1 Effect of operating variables on the extraction of SiO<sub>2</sub> from CFA**

#### **6.3.1.1 Derivation of the model**

Design Expert software (Trial version 7.0.3, Stat-Ease, Inc., Minneapolis, USA) was used to employ CCD which was used to study the main and interactive effects of the operating variables namely; temperature, NaOH concentration, NaOH solution to waste ratio and extraction time on % yield of SiO<sub>2</sub> from CFA. Table 6-1 shows the results obtained from the experiments carried out on extraction of silica from CFA. The relationship between independent variables and response was described by the second-order polynomial (Eq. 6.1).

Table 6-1 Results obtained from the experiments carried out on extraction of silica

| Run | Variable            |                           |                                      |                          |                                     |
|-----|---------------------|---------------------------|--------------------------------------|--------------------------|-------------------------------------|
|     | A: Temperature (°C) | B: NaOH Concentration (M) | C: NaOH Solution: Waste Ratio (mL/g) | D: Extraction Time (min) | Y <sub>CFA</sub> : Silica Yield (%) |
| 1   | 50                  | 1                         | 5                                    | 30                       | 0                                   |
| 2   | 70                  | 2                         | 3.5                                  | 45                       | 14.91                               |
| 3   | 70                  | 4                         | 3.5                                  | 45                       | 43.1                                |
| 4   | 50                  | 1                         | 5                                    | 60                       | 1.5                                 |
| 5   | 70                  | 2                         | 3.5                                  | 45                       | 10.96                               |
| 6   | 70                  | 2                         | 3.5                                  | 75                       | 6.17                                |
| 7   | 90                  | 3                         | 2                                    | 30                       | 10.13                               |
| 8   | 70                  | 2                         | 3.5                                  | 45                       | 5                                   |
| 9   | 70                  | 2                         | 0.5                                  | 45                       | 0                                   |
| 10  | 50                  | 3                         | 2                                    | 30                       | 2.34                                |
| 11  | 70                  | 0                         | 3.5                                  | 45                       | 0                                   |
| 12  | 70                  | 2                         | 3.5                                  | 45                       | 7.13                                |
| 13  | 90                  | 3                         | 5                                    | 30                       | 34.82                               |
| 14  | 70                  | 2                         | 6.5                                  | 45                       | 22.94                               |
| 15  | 110                 | 2                         | 3.5                                  | 45                       | 4.05                                |
| 16  | 70                  | 2                         | 3.5                                  | 45                       | 9.28                                |
| 17  | 50                  | 3                         | 2                                    | 60                       | 6.63                                |
| 18  | 50                  | 1                         | 2                                    | 60                       | 0.87                                |
| 19  | 50                  | 1                         | 2                                    | 30                       | 0                                   |
| 20  | 30                  | 2                         | 3.5                                  | 45                       | 0                                   |
| 21  | 90                  | 1                         | 5                                    | 60                       | 13.96                               |
| 22  | 90                  | 1                         | 5                                    | 30                       | 3.73                                |
| 23  | 70                  | 2                         | 3.5                                  | 15                       | 7.14                                |
| 24  | 90                  | 3                         | 2                                    | 60                       | 12.76                               |
| 25  | 90                  | 3                         | 5                                    | 60                       | 16.41                               |
| 26  | 90                  | 1                         | 2                                    | 30                       | 2.52                                |
| 27  | 50                  | 3                         | 5                                    | 30                       | 22.31                               |
| 28  | 90                  | 1                         | 2                                    | 60                       | 0                                   |
| 29  | 70                  | 2                         | 3.5                                  | 45                       | 5.68                                |
| 30  | 50                  | 3                         | 5                                    | 60                       | 25.96                               |

$$\begin{aligned}
 Y(\%) = & +8.83 + 1.78A + 8.12B + 5.39C + 0.0125D - 0.0600AB + 0.2238AC - 1.15AD \\
 & + 3.24BC - 1.12BD - 0.5187CD - 1.83A^2 + 3.05B^2 + 0.5269C^2 - 0.6796D^2
 \end{aligned}
 \tag{6.1}$$

### 6.3.1.2 Checking the adequacy of the developed model

The statistical significance of the model which describes the extraction of SiO<sub>2</sub> from CFA was evaluated by performing a one-way ANOVA test on the developed models. Table 6-2 shows the results of analysis of variance for SiO<sub>2</sub> extraction in CFA. A close examination of the ANOVA table shows that the regression model has a  $p$ -value of 0.0001, this indicates the statistical significance of the model as a predictive model. A  $p$ -value  $< 0.05$  indicates that there is less than 5% chance that the models the values represent could be due to noise (Ejekwu et al., 2019). The non-significant lack-of-fit with a  $p$  value of 0.1683 ( $>0.05$ ) for the 95% confidence level showed that the quadratic model was valid for the extraction of SiO<sub>2</sub> study (Ejekwu et al., 2019). In addition, the lack of fit F-value of 2.44 implies the lack of fit is not significant relative to the pure error. There is a 16.83% chance that a lack of fit  $f$ -value this large could occur due to noise. Non-significant lack of fit is good, the model needs to fit (Matlob et al., 2012).

Acronym for analysis of variance was used to analyze the effect of individual terms, their interaction and the goodness of the fit of the experimental model (linear and quadratic) (Demir and Derun, 2019). The results in Table 6-2 showed that for the model developed, some terms were significant, and others were not. For the variables to have a significance effect on the response value (SiO<sub>2</sub> extracted), the  $p$ -value has to be less than 0.05. This indicates that the variables were statistically significant at the 95% confidence level, while those with a  $p$ -value greater than 0.05 are not significant (Chitsiga et al., 2018). Additionally, the higher the  $f$ -value for specific independent operating variables, the higher will be the effect of that variable on the response. Although not all the terms were significant, all the terms were considered in the model to minimize the error (Ejekwu et al., 2019). In Table 6-2 B (concentration of NaOH), C (NaOH Solution / Waste Material Ratio), BC (concentration of NaOH\* NaOH Solution / Waste Material Ratio) and B<sup>2</sup> (concentration of NaOH\* concentration of NaOH) have a significant effect on model Eq. 5.1, they impact the SiO<sub>2</sub> extracted from CFA greatly, while the other factors do not. The NaOH concentration has the highest F-value of 58.39, indicating that it has the highest impact on the yield of SiO<sub>2</sub> extracted in CFA. The second highest F-value is that of the NaOH solution to waste ratio of 25.68, indicating that it has the second highest impact on the SiO<sub>2</sub> yield extracted from CFA.

Table 6-2 Analysis of variance of the main and interactive effect of the variables for extraction of SiO<sub>2</sub> in CFA

| Source                                 | Sum of Squares | df | Mean Square | F-value | p-value                       |
|----------------------------------------|----------------|----|-------------|---------|-------------------------------|
| <b>Model</b>                           | 2996.26        | 14 | 214.02      | 7.89    | 0.0001 <b>significant</b>     |
| A-Temperature                          | 76.40          | 1  | 76.40       | 2.82    | 0.1140                        |
| B-Concentration of NaOH                | 1584.05        | 1  | 1584.05     | 58.39   | < 0.0001                      |
| C-NaOH Solution / Waste Material Ratio | 696.82         | 1  | 696.82      | 25.68   | 0.0001                        |
| D-Extraction Time                      | 0.0037         | 1  | 0.0037      | 0.0001  | 0.9908                        |
| AB                                     | 0.0576         | 1  | 0.0576      | 0.0021  | 0.9639                        |
| AC                                     | 0.8010         | 1  | 0.8010      | 0.0295  | 0.8659                        |
| AD                                     | 21.11          | 1  | 21.11       | 0.7783  | 0.3916                        |
| BC                                     | 167.96         | 1  | 167.96      | 6.19    | 0.0251                        |
| BD                                     | 20.07          | 1  | 20.07       | 0.7398  | 0.4033                        |
| CD                                     | 4.31           | 1  | 4.31        | 0.1587  | 0.6960                        |
| A <sup>2</sup>                         | 92.30          | 1  | 92.30       | 3.40    | 0.0850                        |
| B <sup>2</sup>                         | 254.63         | 1  | 254.63      | 9.39    | 0.0079                        |
| C <sup>2</sup>                         | 7.61           | 1  | 7.61        | 0.2807  | 0.6040                        |
| D <sup>2</sup>                         | 12.57          | 1  | 12.57       | 0.4632  | 0.5065                        |
| <b>Residual</b>                        | 406.95         | 15 | 27.13       |         |                               |
| Lack of Fit                            | 337.76         | 10 | 33.78       | 2.44    | 0.1683 <b>not significant</b> |
| Pure Error                             | 69.19          | 5  | 13.84       |         |                               |
| <b>Cor Total</b>                       | 3403.21        | 29 |             |         |                               |

**Table 6-3** shows the mean summary statistics., The high standard deviation and a low R-squared values indicates that there might be some problem with the models or data. Model reduction may

help correct the this. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The adequate precision for the model is greater than 4, it is 11.4210.

Table 6-3 Mean Summary Statistics

| Source                               | Std. Dev. | R-Squared | Adjusted R-Squared | Predicted R-Squared | Adeq. Precision |
|--------------------------------------|-----------|-----------|--------------------|---------------------|-----------------|
| SiO <sub>2</sub> extraction from CFA | 5.21      | 0.8804    | 0.7688             | 0.3991              | 11.4210         |

The  $R^2$  value of 0.8804 (Figure 6-1) was closer to 1, this shows that there is good correlation between the observed and predicted values for SiO<sub>2</sub> extraction from CFA. About 88.04% of the data can be explained and analyzed by the model. While 11.96% of the data cannot be analyzed and explained by the model (Chitsiga et al., 2018).

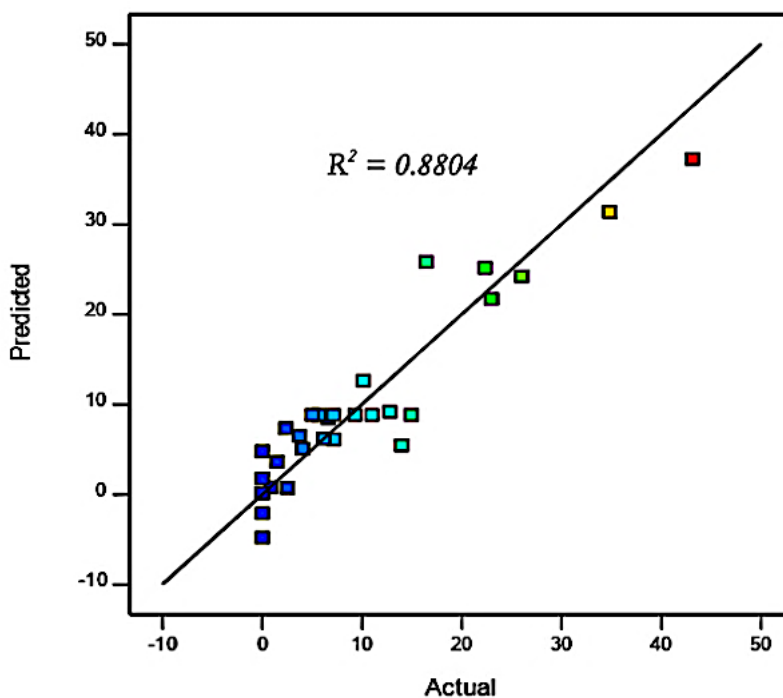


Figure 6-1 Relationship between predicted vs. actual values of responses for the developed model SiO<sub>2</sub> yield from (A) CFA

### 6.3.1.3 Design of experiment and the response surface methodology

In design of experiments and the response surface methodology, the three-dimensional response surface in Figure 6-2, Figure 6-3, Figure 6-4, Figure 6-5, Figure 6-6 and Figure 6-7 show the main and the interaction effects of the considered variables on the extraction of  $\text{SiO}_2$  from CFA. To study the effect of each variable (temperature, NaOH concentration, solution to waste ratio and extraction time), response surfaces were plotted and used to study the interaction effect of the four factors on the extraction of  $\text{SiO}_2$  from the two waste materials.

The general trend is that, as NaOH concentration increases from 1 M to 3 M, the  $\text{SiO}_2$  yield also increased as shown in Figure 6-2. The yield of silica increased from 0% when NaOH was 1M NaOH to 22.31% at 3 M NaOH. This is shown as pink and white circle on the 3D surfaces in Figure 6-2. This trend was also confirmed by Matlob et al. (2012), Rhevi et al. (2014), Setyawan et al. (2019) and Supitcha et al. (2009) in literature, who found that silica yield increases with an increase in the concentration of NaOH. The amount of NaOH also affected the contact area between the waste material (CFA) and solvent. The more solvent, the higher the contact area, so that distribution of solvent to waste material will be even higher. The even distribution of solvents to waste material will increase the formation of  $\text{Na}_2\text{SiO}_3$  and the yield of  $\text{SiO}_2$  obtained (Setyawan et al., 2019).

Similarly, an increase in the NaOH solution to waste ratio from 2 to 5 mL/g resulted in an increase of the  $\text{SiO}_2$  yield extracted from CFA as shown in Figure 6-3. The yield of silica increased from 10.13% when the NaOH solution waste ratio is 2 mL/g to 34.82% at a solution to waste ratio of 5 mL/g. This is shown as red and white circle on the 3D surfaces in Figure 6-3. This trend was also confirmed by Setyawan et al. (2019) in literature. The reason an increase in the NaOH solution to waste ratio yield more silica is that it favors the dissolution rate, which can be explained by an increase in the amount of free NaOH and lower viscosity during the reaction (Xiao et al., 2010).

An increase in temperature from 50 to 90 °C, resulted in an increase in the  $\text{SiO}_2$  yield (see Figure 6-2B, and Figure 6-3B). The yield of silica increased from 22.31% (shown as pink and white circle in the 3D surface) at 50 °C to 34.82% (shown as pink and white circle in the 3D surface) at 90 °C.

A higher SiO<sub>2</sub> yield at higher temperatures was attributed to the fact that molecules at higher temperatures have more thermal energy required for effective reaction (Shemi, 2013).

An increase in silica extraction time from 30 to 60 min, resulted in an increase in the SiO<sub>2</sub> extracted from CFA as shown in Figure 6-4. The yield of silica increased from 0% at an extraction time of 30 to 0.87% at an extraction time of 60 min (shown as red and white circle in the 3D surfaces). A prolonged exposure of the solid waste in the solvent, allows adequate time for desired compounds to migrate into the solvent (Che Sulaiman et al., 2017).

The interaction between temperature and NaOH concentration, showed that when the two variables increase, the SiO<sub>2</sub> yield also increases (Figure 6-2A and 6-3B) (Setyawan et al., 2019). The yield increased from 0% (Figure 6-2A, where the operating conditions were; 50 °C, 1 M NaOH, 5 mL/g NaOH solution to waste ratio and 30 min extraction time) to 34,82% (Figure 6-3B, where the operating conditions were; 90 °C, 3 M NaOH, 5 mL/g NaOH solution to waste ratio and 30 min extraction time). The NaOH concentration increased from 1 M to 3 M and the temperature increased from 50 °C to 90 °C.

The interaction between NaOH concentration and NaOH solution to waste ratio showed that with an increase in the two variables, the SiO<sub>2</sub> yield also increased (Figure 6-4A and Figure 6-2B) (Setyawan et al., 2019). The yield increased from 0% (Figure 6-4A, where the operating conditions were; 50 °C, 1 M NaOH, 2 mL/g NaOH solution to waste ratio and 30 min extraction time) to 22,31% (Figure 6-2B, where the operating conditions were; 50 °C, 3 M NaOH, 5 mL/g NaOH solution to waste ratio and 30 min extraction time). The NaOH concentration increased from 1 M to 3 M and the NaOH solution to waste ratio increased from 2 mL/g to 5 mL/g.

The interaction between temperature, NaOH concentration, NaOH solution to waste ratio and extraction time showed that with maximum NaOH concentration, solution to waste ratio and temperature (3 M, 5 mL/g and 90 °C) at minimum extraction time (30 min), a high SiO<sub>2</sub> yield of 34.82% was observed (see Figure 6-3B). With maximum NaOH concentration, NaOH solution to waste ratio and extraction time (3 M, 5 mL/g, 60 min) at minimum temperature (50 °C), a high SiO<sub>2</sub> yield of 25.96% was observed. for CFA (see Figure 6-5). This means that a simultaneous

increase in temperature and time, results in a decrease in the yield of  $\text{SiO}_2$  extracted (see Figure 6-2B and Figure 6-6). Increasing temperature from 50 to 90 °C and the silica extraction time from 30 to 60 min decreased the silica yield from 22.31% (Figure 6-2B) to 16.41% (Figure 6-6).

NaOH concentration and NaOH solution to waste ratio had the greatest impact on the yield of  $\text{SiO}_2$ , when they were at their maximum 3 M and 5 mL/g, respectively) and temperature and extraction time at their minimum (50 °C and 30 min, respectively), they yielded a high yield of 22.31% (Figure 6-2B). When NaOH concentration, NaOH solution to waste ratio were at their minimum and temperature and time at their maximum, no silica was produced (Figure 6-7).

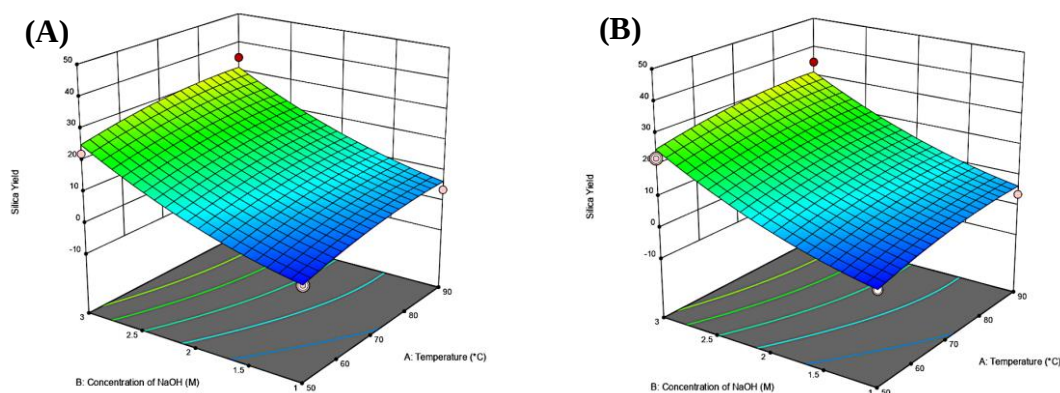


Figure 6-2 3D response surfaces of the extraction of  $\text{SiO}_2$  from CFA at 50 °C, 30 min extraction time, 5 mL/g solution to waste ratio at (A) 1 M NaOH and (B) 3 M NaOH

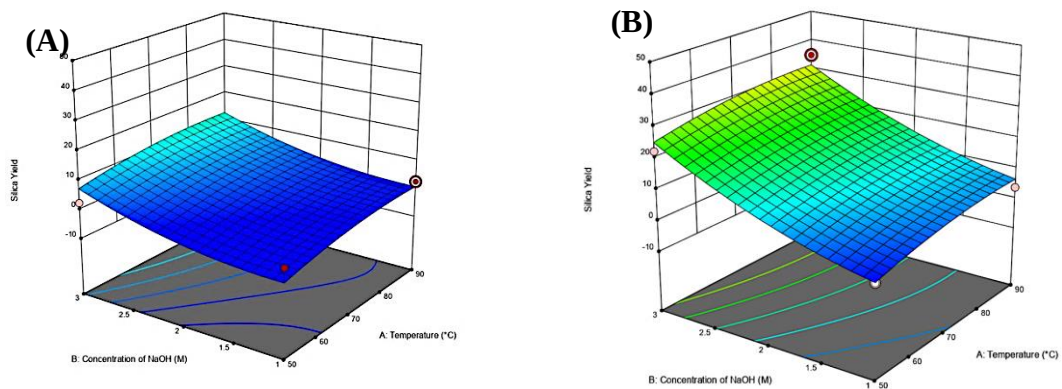


Figure 6-3 3D response surfaces of the extraction of  $\text{SiO}_2$  from CFA at 90 °C, 30 min extraction time, 3 M NaOH at a solution to waste ratio of (A) 2 mL/g and (B) 5 mL/g

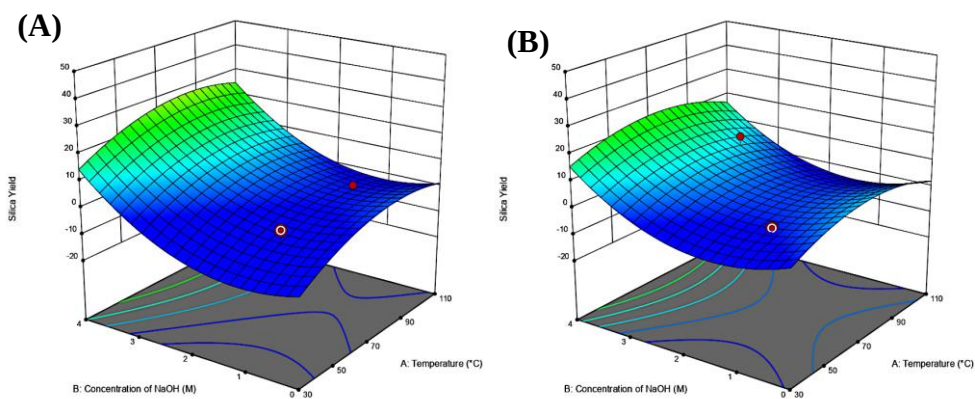


Figure 6-4 3D response surfaces of the extraction of  $\text{SiO}_2$  from CFA at 50 °C, 1 M NaOH, 2 mL/g NaOH solution, at an extraction time of (A) 30 min and (B) 60 min

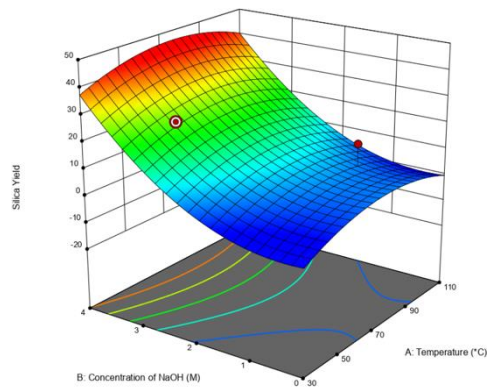


Figure 6-5 3D response surfaces of the extraction of  $\text{SiO}_2$  from CFA at 50 °C, 3 M NaOH, 5 mL/g NaOH solution, at an extraction time of 60 min

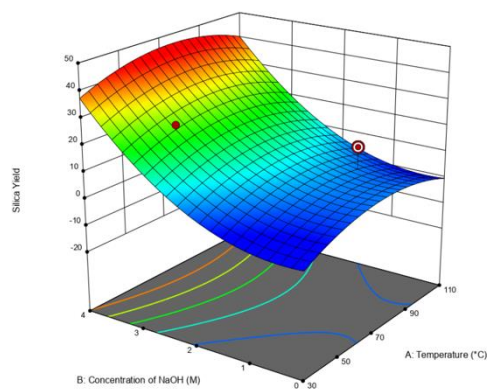


Figure 6-6 3D response surfaces of the extraction of  $\text{SiO}_2$  from CFA at 90 °C, 3 M NaOH, 5 mL/g NaOH solution, at an extraction time of 60 min

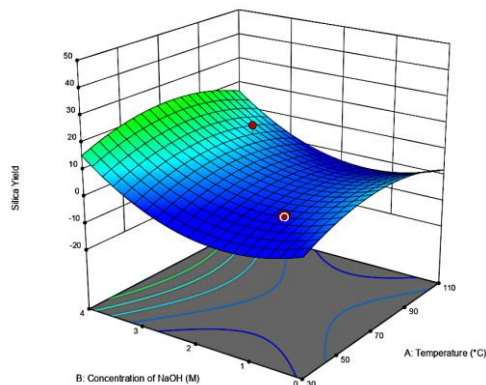


Figure 6-7 3D response surfaces of the extraction of SiO<sub>2</sub> from CFA at 90 °C, 1 M NaOH, 2 mL/g NaOH solution, at an extraction time of 60 min

### 6.3.2 Optimization by desirability function

To optimize the model response (silica yield) in CFA, the mathematical model developed was used to determine experimental conditions (temperature, NaOH concentration, NaOH solution to waste ratio and extraction time) to be used. Desirability Function (DF) is an objective function that is scaled to be between 0 and 1. To maximize the desirability function, a suitable point is found using numerical optimization (Akçay and Anagün, 2013). Figure 6-8 was obtained from design expert; it shows the optimum extraction conditions for CFA.

The optimum conditions found for SiO<sub>2</sub> extraction from CFA using numerical optimization by desirability function were: 86.69 °C, 3 M NaOH concentration, 5 mL/g NaOH solution to waste material ratio and 30 min for SiO<sub>2</sub> yield of 31.40%.

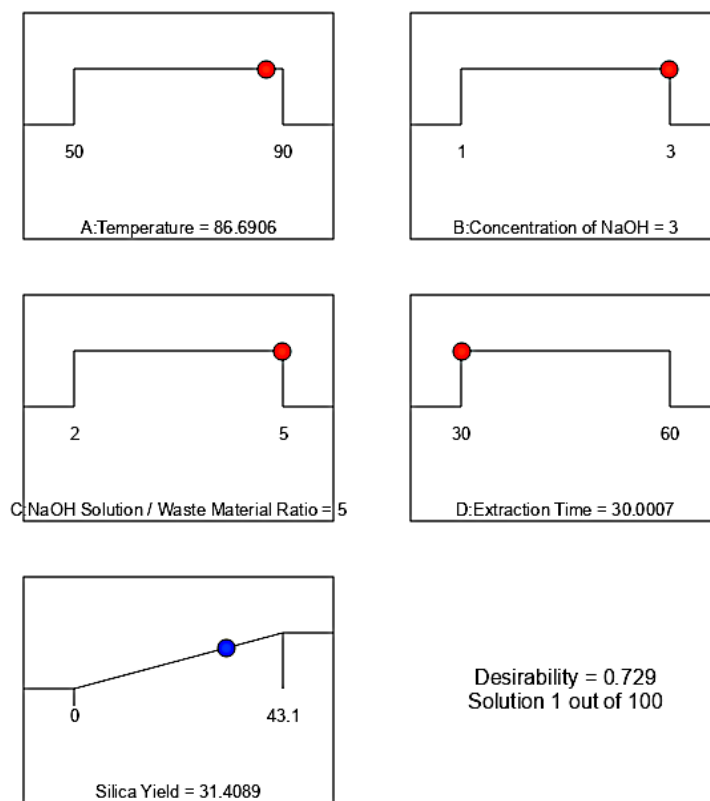


Figure 6-8 Desirability ramp of SiO<sub>2</sub> extraction from CFA

### 6.3.3 Validation of the model predicted optimal conditions

In order to test the validity of the optimized conditions given by the model, replicated experiments were carried out with parameters suggested by the model. The conditions used in the confirmatory experiments were as follows: temperature (86.69 °C), NaOH concentration (3 M), NaOH solution to waste material ratio (5 mL/g NaOH) and time (30 min).

The actual yield of SiO<sub>2</sub> extracted from CFA was found to be 31.06% (Table 6-4), which is consistent with the model. With an error margin of 1.11% between the predicted value and the confirmatory test value. The results of the optimized SiO<sub>2</sub> yield show the accuracy of the developed model. The optimized results of SiO<sub>2</sub> extracted from CFA are relatively low from that of Matlob et al. (2012) of 42.3%. The reason for this could be because they used 4 M of NaOH instead of 3 NaOH. They found that silica yield was low at NaOH concentration between 2–3.5 M, while a high yield was obtained between 4.5–6 M (Matlob et al., 2012). The model of SiO<sub>2</sub> extraction from CFA fits the experimental data very well, this shows the accuracy of the developed model.

Therefore, the SiO<sub>2</sub> yield extracted from CFA for any combination of temperature, NaOH concentration, NaOH solution to waste material ratio and extraction time, could accurately be predicted by the regression model obtained by RSM (Aydar, 2018).

Table 6-4 Silica extraction at optimum conditions

| Parameter |                      | Temperature<br>(°C) | NaOH<br>concentration<br>(M) | NaOH solution<br>to waste material<br>ratio (mL/g) | Time (min) | % SiO <sub>2</sub><br>extraction |
|-----------|----------------------|---------------------|------------------------------|----------------------------------------------------|------------|----------------------------------|
| CFA       | Model                | 87                  | 3                            | 5                                                  | 30         | 31.41                            |
|           | Confirmatory<br>test | 87                  | 3                            | 5                                                  | 30         | 31.06%                           |

## 6.4 Physico-chemical properties of optimized SiO<sub>2</sub> from CFA

### 6.4.1 FESEM-EDX analysis of the optimized extracted silica from CFA

Figure 6-9 shows the FE-SEM image and the EDS spectrum of the amorphous optimized SiO<sub>2</sub> extracted from CFA. Like the FE-SEM images in Chapter 5 (Section), it is similar to the FE-SEM images of SiO<sub>2</sub> extracted by Music et al. (2011) and Kaduku et al. (2015). The EDS spectrum showed the presence of silicon and oxygen, confirming this is indeed SiO<sub>2</sub> which was precipitated from CFA. The EDS spectrum also showed the presence of sodium, chloride and aluminum ions, this indicates that the ions were not well removed in their mother liquor (Music et al., 2011). The presence of the low amount of carbon could be from CFA (Adam et al., 2011). The reason for this could be due to the method used in the extraction of silica, impurities were not properly removed. In order to extract SiO<sub>2</sub>, Azat et al. (2019), Kaduku et al. (2015) and Music et al. (2011) leached twice, using acid leaching and alkaline leaching. This is to ensure that metal oxides such as CaO and Al<sub>2</sub>O<sub>3</sub> were thoroughly removed. In this study, only alkaline leaching was done, which may also be the cause of the impurities in CFA.

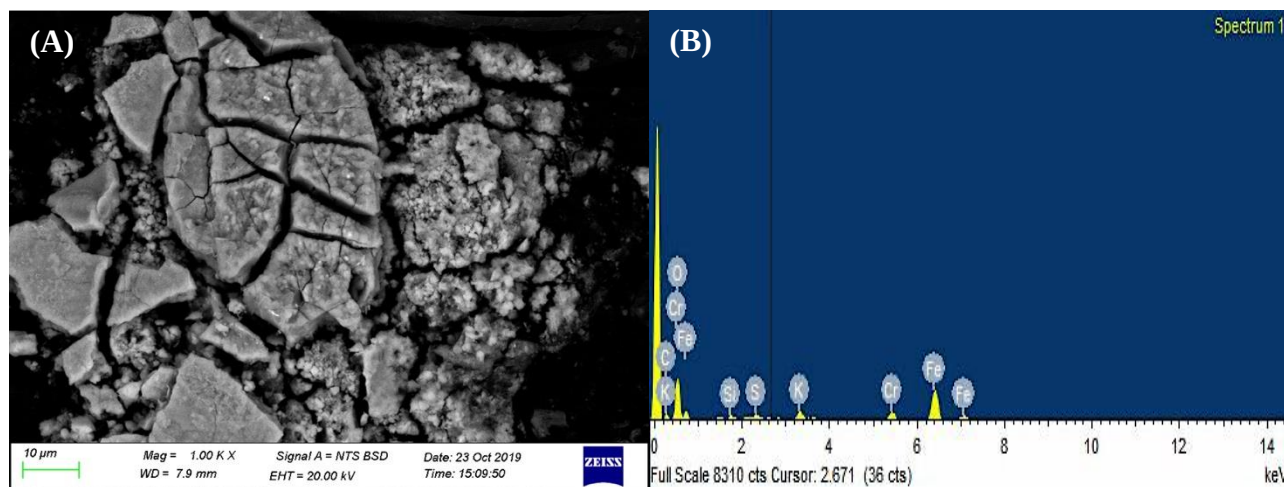


Figure 6-9 (A) Morphology and (B) Spectrum of optimized silica extracted from CFA

#### 6.4.2 Thermogravimetric analysis results of optimized $\text{SiO}_2$ extracted from CFA

The TGA weight loss curve for the optimized  $\text{SiO}_2$  extracted from CFA is shown in Figure 6-10. A weight loss at just above 21  $^{\circ}\text{C}$  is observed. This is due to the evaporation of physically adsorbed water molecules (Lin and Zhou, 2017). This low temperature weight loss is also similar to the commercial  $\text{SiO}_2$  reported in literature (Lin and Zhou, 2017; Ivan et al. 2003). A total weight loss of about 48 wt% is observed. The above results indicate that the  $\text{SiO}_2$  extracted from the two wastes materials are thermally stable only at lower temperatures and can be used up to 20  $^{\circ}\text{C}$  only (Arora et al., 2018).

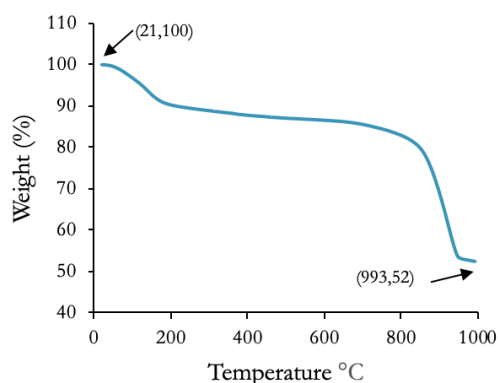


Figure 6-10 TGA weight loss (%) vs Temperature ( $^{\circ}\text{C}$ ) curves of optimized  $\text{SiO}_2$  extracted CFA

## 6.5 Concluding remarks

In this chapter the objective was to optimize the four parameters, namely; temperature, NaOH concentration, NaOH solution to waste material ratio and extraction time. To achieve this optimization experiments were designed using central composite design (CCD) and response surface methodology (RSM) in order to determine the optimal set of the four parameters.

A second order quadratic model for  $\text{SiO}_2$  extraction in CFA was developed for factor optimization using computer simulation software (Trial version 7.0.3, Stat-Ease, Inc., Minneapolis, USA) by applying least of squares method based on the experimental design. A fitted predictive model was developed as mathematical expression of  $\text{SiO}_2$  extraction from CFA by collecting the data using central composite design. Analysis of variance (ANOVA) was then used to study the effect of each individual variables as well as the joint interactive effects on silica extraction from coal fly ash.

The investigation of the parametric effect showed that all four variables considered in the study had a strong influence on the yield of  $\text{SiO}_2$  extraction from CFA. The interaction of the NaOH concentration and NaOH solution to waste ratio had the greatest influence on the  $\text{SiO}_2$  yield, with their increase, an increase in the  $\text{SiO}_2$  yield was also observed, even at minimum temperature and extraction time.

The optimum conditions found for  $\text{SiO}_2$  extraction from CFA using numerical optimization by desirability function were: 86.69 °C, 3 M NaOH concentration, 5 ml/g NaOH solution to waste material ratio and 30 min for  $\text{SiO}_2$  yield of 31.40%.

The actual silica obtained was 31.06%, giving a margin error of 1.11%, with a linear correlation coefficient of 88.04%, thus, verifying that good fitting of experimental data and fitness of the model.

The FE-SEM results indicated that extracted product is indeed silica. The TGA results indicated that the optimized silica is stable in a temperature below 21 °C.

## Chapter 7: Kinetics of Silica Extraction from CFA

### 7.1 Introduction

This chapter discusses the results obtained for the kinetic study of the extraction of SiO<sub>2</sub> from CFA.

### 7.2 Experimental

The detailed method applied to perform the kinetic study of the extraction of silica from CFA is detailed in Chapter 3 (Section 3.8 – 3.9) of this Thesis.

### 7.3 Results and discussion

#### 7.3.1 Extraction kinetics of SiO<sub>2</sub> from CFA

The experimental data of SiO<sub>2</sub> yield from CFA versus time at varying reaction temperatures to obtain the reaction rate constant ( $k$ ) is shown in Figure 7-1. Figure 7-1 shows the fit model and experimental data for silica yield extracted from CFA at 50 °C, 60 °C, 70 °C and 80 °C using a solution to waste ratio of 5 mL/g, 3 M NaOH,  $\omega_{stir\ bar} = 250\ rpm$ . The results showed a general trend, where an increase in the extraction time resulted in an increase in SiO<sub>2</sub> yield. The reason for this is that a prolonged exposure of the solid waste in the solvent allows adequate time for desired compounds to migrate into the solvent (Che Sulaiman et al., 2017). The results also showed that SiO<sub>2</sub> yield increases with an increase in temperature, 80 °C yielding the highest silica. The reason the SiO<sub>2</sub> yield increases with an increase in temperature is that molecules at high temperatures have more thermal energy required for effective reaction (Shermi, 2013). This trend was also witnessed by Baumer et al. (2010), dos Santos et al. (2015) and Rezazi et al. (2017), who also witnessed that the yield increases with an increase in temperature and contact time. Minimum SiO<sub>2</sub> yield is found at 50 °C, the second smallest yield is found at 70 °C, then the third smallest yield is at 60 °C and the highest yield is at 80 °C. So, the SiO<sub>2</sub> yield in CFA increased in the following manner 50 °C < 70 °C < 60 °C < 80 °C (Figure 7-1). The reason the SiO<sub>2</sub> yield at 60 °C was higher than the one at 70 °C could be due to error caused by the propagation errors of the measuring device (Ejekwu et al., 2019).

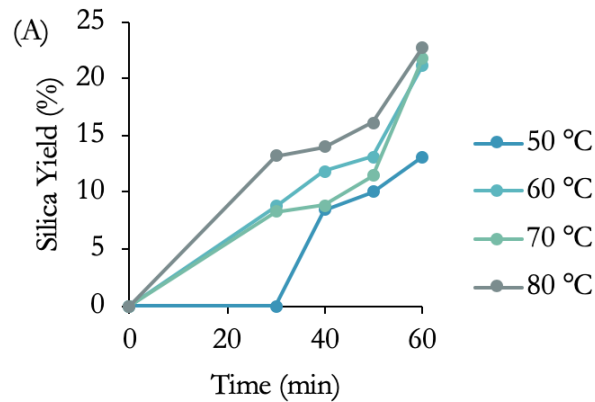


Figure 7-1 The effect of temperature and time on SiO<sub>2</sub> extraction from CFA at liquid to solution to waste ratio of 5 mL/g, 3 M NaOH,  $\omega_{stir\ bar} = 250$  rpm

### 7.3.2 Reaction rates of SiO<sub>2</sub> extraction from CFA

The experimental results obtained for SiO<sub>2</sub> extracted from CFA were fitted to an integrated pseudo first-order rate kinetics (Eq. 3.8). Figure 7-2 shows the plots of the natural log of the silica yield versus extraction time at 50 °C, 60 °C, 70 °C and 80 °C, at liquid to ratio of 5 mL/g, 3 M NaOH,  $\omega_{stir\ bar} = 250$  rpm. From the plots the rate constant 'k' was estimated using the straight line that resulted. The straight line obtained for each temperature (50 – 80 °C), suggested a first order rate for the SiO<sub>2</sub> extraction. The correlation coefficient 'R' and the rate constant 'k' for each plot is presented in Table 7-1.

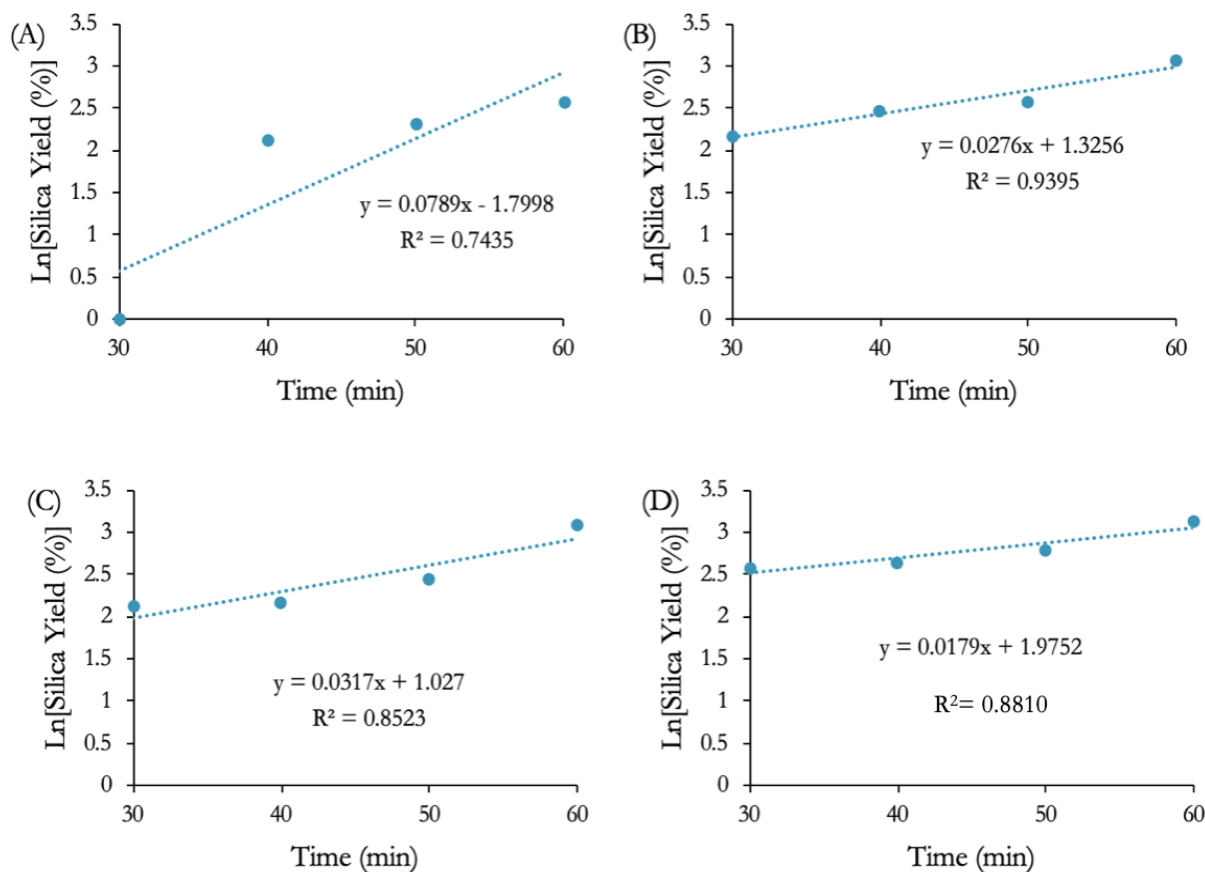


Figure 7-2 Kinetics of extraction of SiO<sub>2</sub> from CFA at (A) 50 °C, (B) 60 °C, (C) 70 °C, (D) 80 °C at a liquid to ratio of 5 mL/g, 3 M NaOH,  $\omega_{\text{stir bar}} = 250$  rpm

Table 7-1 shows the results of the estimated kinetic constants for the extraction of SiO<sub>2</sub> from CFA. Notably, the relationship between the kinetic constant and temperature is not observed. The rate constant does not increase with an increase in temperature. The reason for this might be due to measurement error of the mercury thermometer that was used to measure the SiO<sub>2</sub> extraction temperature. The response time of the thermometer might have been delayed detecting the change in temperature from room temperature, hence giving inaccurate results. The thermometer used was also marked off in 10th's of a degree, thus could only be measured to that degree of accuracy. The higher the rate constant the faster the rate of SiO<sub>2</sub> extraction (Ejekwu et al., 2019). The higher the temperature the faster the rate of extraction (dos Santos et al., 2015) The reason for this is that increasing the temperature of a system increases the average kinetic energy of its constituent

particles. As the average kinetic energy increases, the particles move faster and collide more frequently per unit time and possess greater energy when they collide. Both these factors increase the rate of reaction. Hence the reaction rate of virtually all reactions increases with increasing temperature. According to the results obtained, the fastest SiO<sub>2</sub> extraction from CFA was at 50 °C and the slowest SiO<sub>2</sub> extraction occurred at 80 °C. These results did not agree with what other authors witnessed in literature. Other authors witnessed that the rate of extraction increases with an increase in temperature (dos Santos et al., 2015; Mosca et al., 2018). The reason for this might be due to the method of SiO<sub>2</sub> extraction which resulted in a margin error. In Chapter 4, it was found that the SiO<sub>2</sub> extracted from the CFA was recovered with some contaminants due to the method used. The error might also be due to the propagation errors of the measuring devices (Ejekwu et al., 2019). The R<sup>2</sup> values indicate good fit, they all had an R<sup>2</sup> > 0.7. This means over 70 % of the data can be explained by the model. This also means that the regression model account for over 70% of the variance.

Table 7-1 Estimated kinetics constants for SiO<sub>2</sub> extraction

| <b>T(k)</b> | <b>CFA</b>                |                      |
|-------------|---------------------------|----------------------|
|             | <b>k (s<sup>-1</sup>)</b> | <b>R<sup>2</sup></b> |
| 323         | 0.0789                    | 0.7435               |
| 333         | 0.0276                    | 0.9395               |
| 343         | 0.0317                    | 0.8523               |
| 353         | 0.0179                    | 0.8810               |

### 7.3.3 Activation energy and frequency factor determination

The natural logarithm of k values at different experimental temperatures are plotted versus the inverse temperature (1/T) to determine the activation energy (E<sub>a</sub>) and frequency factor (A) for the extraction of SiO<sub>2</sub> reactions using Eq. 3.10. Figure 7-3 present the plot of the rate constant fitted with the Arrhenius equation.

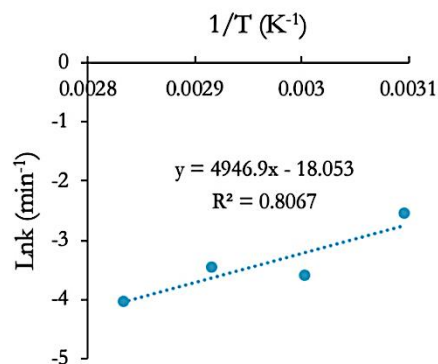


Figure 7-3 Arrhenius plot based on apparent component extraction rate constant ( $k$ ) at temperatures from 50 – 80 °C

The activation energy ( $E_a$ ) of the extraction of  $\text{SiO}_2$  and frequency factors ( $A$ ) were obtained from the slope and the intercept of  $\ln k$  vs.  $1/T$  plot, respectively. The frequency factors and the activation energy are shown in Table 7-2.

The activation energy and frequency factor for the extraction of  $\text{SiO}_2$  in CFA are  $4946.9 \text{ J.mol}^{-1}$  and  $18.053 \text{ min}^{-1}$ , respectively. This indicates that the minimum energy required to initiate the extraction of  $\text{SiO}_2$  from CFA is  $4946.9 \text{ J.mol}^{-1}$ . The  $R^2$  (0.8067) value indicates that the Arrhenius equation correlates the rate with temperature quite well. Furthermore, the equation provides a useful method for graphically determining the activation energy of  $\text{SiO}_2$  extraction from CFA if the rates at various temperatures are known. Chemical reactions have activation energies of more than  $45\,000 \text{ J.mol}^{-1}$  (Valeev et al., 2018; Xiao et al., 2010). This means that the  $\text{SiO}_2$  extraction process from CFA is controlled by chemical reaction steps.

Table 7-2 The activation energy parameters for  $\text{SiO}_2$  extraction

| Waste Material | A ( $\text{min}^{-1}$ ) | $E_a$ ( $\text{J.mol}^{-1}$ ) | Arrhenius Fit, $R^2$ |
|----------------|-------------------------|-------------------------------|----------------------|
| CFA            | 18.053                  | 4946.9                        | 0.8067               |

#### 7.4 Concluding remarks

A high activation energy was obtained, this correlates with the temperature dependents of  $\text{SiO}_2$  extraction CFA. The results above showed that  $\text{SiO}_2$  extraction from CFA followed a first order reaction kinetics while  $\text{SiO}_2$ .

## Chapter Eight: General Conclusion and Recommendations

### 8.1 Conclusion

The aim of this study was to extract  $\text{SiO}_2$  from CFA and PWA and to optimize the  $\text{SiO}_2$  extraction from CFA. Therefore, the following conclusions are drawn from this current study:

- $\text{SiO}_2$  was successfully extracted from the two wastes materials. Although CFA possess a high  $\text{SiO}_2$  percentage, in the same extraction conditions and method, PWA extracted a high yield of  $\text{SiO}_2$ . The analytical study of the  $\text{SiO}_2$  extracted from CFA and PWA using alkaline leaching prove that the material extracted from the two-waste materials is indeed  $\text{SiO}_2$ .
- The parametric study using response surface methodology indicated that the factors which were investigated were indeed significant to the  $\text{SiO}_2$  yield extracted from the CFA. They also showed that the interaction of the NaOH solution and the NaOH solution to waste ratio had the highest impact on the yield of  $\text{SiO}_2$ . Using numerical optimization by desirability function, optimum silica extraction conditions were: 86.69 °C, 3 M NaOH concentration, 5 mL/g NaOH solution to waste material ratio and 30 min for  $\text{SiO}_2$  yield of 31.40%. The actual  $\text{SiO}_2$  yield was found to be 31.06%.
- The kinetic study results showed that the process of the extraction of  $\text{SiO}_2$  from CFA, followed a first-order reaction kinetics.

Thus, the encouraging results obtained from this thesis could provide a platform for the beneficiation of these waste material. This would not only lower the amount of PW and CFA that goes into landfills but would subsequently reduce the costs that goes into managing the landfills and the energy that is used to manufacture quartz.

### 8.2 Recommendations

Based on the observations from this study, the following suggestions need to be considered in the development of a new technique for extraction of silica from industrial waste materials:

- As mentioned in Chapter 4, the  $\text{SiO}_2$  extracted from CFA and PWA is not completely pure. The method used is not sufficient enough to remove all the metal impurities. Acid leaching with an organic acid must be employed in order to produce pure  $\text{SiO}_2$ . It is hypothesized that the extraction yields could be slightly increased with adjustment of the SET conditions.
- Maintaining constant NaOH concentration at higher temperature was a challenge during this study due to expected evaporation at higher temperature. This should be taken into account in future work.
- Model reduction is required in order to improve the predicted model

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