

ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

Synthesis, Extraction and Optimization of Silica Production from Teff straw (*Eragrostis tef*)

A Thesis submitted to Addis Ababa Institute of Technology, In Partial Fulfillment of the requirement of degree of Master of Science in chemical Engineering (Process Engineering Stream)

By: Feven Hagereselam

Advisor: Dr. Shegaw A.

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ADDIS ABABA INSTITUTE OF TECHNOLOGY (AAiT)

SCHOOL OF CHEMICAL AND BIO- ENGINEERING

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Approved By the Examining Board	Signatures	Date
_____	_____	_____
(Chair, Department Graduate Committee)		
_____	_____	_____
(Advisor)		
_____	_____	_____
(Internal Examiner)		
_____	_____	_____
(External Examiner)		

DECLARATION

I declare that this thesis for the M.Sc. Degree at Addis Ababa University, hereby submitted by me, is my original work and has not previously been submitted for the degree at this or any other university, and that all resources of materials used in this thesis have been duly acknowledged.

Name: Feven Hagereselam

Signature: _____

Date of Submission: _____

This thesis has been submitted for examination with my approval as University Advisor.

Name:

Signature: _____

Date: _____

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Table of Contents

ACKNOWLEDGMENT i

List of Figures v

List of Tables vi

List of Acronyms vii

Abstract viii

CHAPTER ONE 1

1. Introduction 1

1.1. Background 1

1.2. Statement of the problem 4

1.3. Objective 5

1.3.1 General objective 5

1.3.2 Specific objectives 5

1.4 Significance of the Study 5

CHAPTER TWO 6

2. Literature Review 6

2.1. Sources of Silica 6

2.2. Amorphous Silica 6

2.2.1. Types of amorphous silica 7

2.3. Application of Amorphous Silica 10

2.4 Crystalline Silica 12

2.5 Silica Production from Organic Waste 13

2.6 Teff *(Eragrostis tef)* and Teff Straw 15

2.7 Surface Chemistry of Amorphous Silica 17

2.8 Silica Processing Methods 19

2.8.1 Conventional Silica Processing Method 19

2.8.2 Silica Processing Methods from Biomass 19

2.9 Thermal Treatment Technologies 21
2.10 Parameters affecting Silica Production from Teff Straw 24
2.10.1 Burning Temperature 24
2.10.2 NaOH Concentration and Extraction Time 25
2.10.3 The pH of Precipitator Acid 26
2.10.4 The Aging Time 26
CHAPTER THREE 27
3. Materials and Methods 27
3.1 Materials 27
3.1.1 Raw Materials 27
3.1.2 Chemicals 27
3.1.3 Equipment 27
3.2 Methods 28
3.2.1 Sample collection 28
3.2.2 Raw Material Analysis 28
3.2.3 Sample Preparation 29
3.2.4 Teff Straw Ash Preparation 31
3.2.5 Bio Silica Extraction 32
3.2.6 Bio Silica Gel Preparation 33
3.2.7 Chemical characterization of TSA and TSAS 35
3.2.8 Silica Yield Calculation 36
3.2.10 Experimental Design 36
3.2.11 Methyl Orange Adsorption Experiment 38
CHAPTER FOUR 39
4. Result and Discussion 39
4.1 Raw Material Characterization 39
4.1.1 Moisture Content of the Raw Teff Straw 39

4.1.2 Determination of Ash Content 39
4.2 Reaction Mechanism 40
4.3 Characterization of the TSA and Extracted Silica 41
4.3.1 Chemical Content Analysis of the Teff Straw Ash 41
4.3.2 Fourier Transform Spectroscopy (FTIR) 42
4.3.3 X-Ray Diffraction (XRD) 43
4.4 Silica Yield Result and Effect of Process Parameters on the Extraction of Silica 44
4.4.1 Silica Yield 44
4.4.2 Statistical Analysis for the yield of silica 45
4.4.3 Model Adequacy Check 48
4.4.3 The Effect of NaOH Concentration on the Extraction of Silica 49
4.4.4 The Effect Extraction Time on the Extraction of Silica 50
4.4.5 The Effect Extraction Temperature on the Extraction of Silica 51
4.4.6 Interaction Effect on the Yield of Silica 52
4.4.7 Optimal Silica Yield Process Parameters to Prepare Maximum Silica Yield 53
4.5 Methylene Orange Adsorption 54
CHAPTER FIVE 56
5. Conclusion and Recommendation 56
5.1 Conclusion 56
5.2 Recommendation 57
Appendices 61

List of Figures

Figure 2. 1 The effect of pH on gel time and the BET surface area of a gel (C. Setzer 2002) 10
Figure 2. 2 structure of crystalline silica 13
Figure 2. 3 (A) X-ray diffraction (XRD) spectra of synthesized biosilica samples (B) FTIR spectra of synthesized biosilica samples. (Bageru and Srivastava 2018) 15
Figure 2. 4 (A) teff pant (B) mass of teff straw (Refera 2001) 16
Figure 2. 5 Structure of Amorphous Silica (C. Setzer 2002) 18
Figure 2. 6 Types of Silanol Groups (C. Setzer 2002) 18

Figure 3. 1 Soaking of Teff Straw in Tap Water 29
Figure 3. 2 Sun Drying of Washed Teff Straw 30
Figure 3. 3 Acid Leaching 31
Figure 3. 4 Washed and Filtered Teff Straw 31
Figure 3. 5 (A) Ashing process in muffle furnace (B) Calicined teff straw ash 32
Figure 3. 6 (A) unfiltered sodium silicate solution (B) filtrated sodium silicate solution 33
Figure 3. 7 (A) Gelification (B) cooling (C) aging (D) filtered silica gel (E) dried silica 34
Figure 3. 8 Experimental flow sheet diagrams of bio silica preparation 35

Figure 4. 1 FTIR spectra of synthesized silica from teff straw 43
Figure 4. 2 XRD pattern of silica sample from teff straw 44
Figure 4. 3 Predicted versus the actual yield of silica 48
Figure 4. 4 Effect of NaOH concentrations on the extraction of silica 49
Figure 4. 5 Effect Extraction Time on the Extraction of Silica 51
Figure 4. 6 Effect of temperature on the extraction of silica 51
Figure 4. 7 (A) interaction effect between NaOH concentration and extraction time, (B) interaction effect between NaOH concentration and extraction temperature and (C) interaction effect between extraction time and extraction temperature 53
Figure 4. 8 Optimization constraints and solutions for extraction of silica 54
Figure 4. 9 Methyl Orange Concentrations versus Adsorption 55

List of Tables

Table 2. 1 XRF result of teff straw (ffff) 17
Table 2. 2 Infrared band assignments of silica 18

Table 3. 1 Experimental levels and factors with design expert version 11 37

Table 4. 1 Moisture content of raw teff straw 39
Table 4. 2 Ash content of teff straw 40
Table 4. 3 Chemical composition of TSA 41
Table 4. 4 Experimental silica yield from teff straw 44
Table 4. 5 ANOVA of fitted model for the yield of bio silica 45
Table 4. 6 Modified ANOVA of fitted model for the yield of bio silica 47
Table 4. 7 Adsorption result 54
Table 4. 8 Treated methyl orange adsorption result 55

List of Acronyms

ANOVA	Analysis of Variance
BC	Before Christ
DF	Degree of Freedom
FTIR	Fourier Transform Infrared
XRD	X-ray diffraction
Rpm	Revolution per minute
AAS	Atomic absorption spectrophotometer
TSA	teff straw ash
LOI	loss on ignition
PDF	powder diffraction files
SSS	Sodium Silicate Solution
ICSD	International Center for Diffraction Data
TEOS	tetraethoxysilane
TMOS	tetramethoxysilane

Abstract

Silica is one of the important chemicals widely used in manufacturing sectors for different applications. Some of the applications of silica are in detergents and cleaners as extenders, in rubber and tire as fillers, in shoe sols, Ink-receptive Coatings, adsorptive, adhesive and others. As the commercial silica is produced from non-renewable, and there are some ongoing issues with health hazard due to the crystalline structure of the raw material which is quartz and high emission of carbon dioxide and waste water, the purpose of this research was to develop bio-based silica using teff straw as a renewable feed stock. This study reports preparation of silica from teff straw ash by sol-gel method. The process of bio-silica production includes leaching of teff straw with 2.5N of HCl acid. The treated teff straw was decomposed thermally at ashing temperature 700°C for 2 hours. Before proceeding to the extraction of silica using alkali solution the silica percentage in the ash was analyzed using AAS spectrometer. The ash was treated with NaOH solution at different concentration (0.5M, 1.5M and 2.5M), different extraction time (60min, 90min and 120 min) and various extraction temperatures (75^0C, 85^0C and95^0C) prior to acidification in order to extract silica in the form of sodium silicate solution (SSS). Design Expert® version11.1.0.1 with Box-Behenken was applied to investigate the effect of experimental variables. Significance of the process variables were analyzed by ANOVA. The optimum parameters for the extraction of amorphous silica were 1.79M of NaOH, 109.99 minutes and 84.17^0C with maximum yield of 83.23%. Physicochemical properties of extracted silica were determined by performing XRD and FTIR analysis. The teff straw ash contains about 92% silica.

CHAPTER ONE

1. Introduction

1.1. Background

Teff, (*Eragrostis tef*) Trotter is a staple food crop in Ethiopia. It has existed in Ethiopia since recorded history of the country and some authorities believed that the pre-Semitic inhabitants might have domesticated it in BC. Teff originated and has diversified in Ethiopia. Tef accounts for about two-third of the daily protein intake in the diet of the population. Teff grain is used mostly for a traditional food called *Enjera* (pancake- like flat bread) and for making porridge. Teff grain is also used for preparing traditional alcoholic drinks called *Arak'e* and *T'ella*(Bultosa 2007).

In terms of ranking by annual cereal crop production in Ethiopia, teff is the third (after maize and wheat) in terms of annual grain production. Physically, teff is a fine-stemmed and tufted annual grass characterized by a large crown, a shallow diverse root, and many shoots system. Its grain has oval shape with size of 0.7–1.0 mm diameter and 0.9–1.7 mm length. The mass of individual teff grain ranges from 0.2 to 0.4 mg whereas 1 g of teff contains 2500–3000 seeds. One hundred fifty teff grains weigh as much as one grain of wheat which makes it the smallest grain in the world among carbohydrate-rich kernels (Bultosa 2007).

After Teff grain is threshed, the straw is used as animal feed especially during the dry season. Farmers feed teff straw preferentially to milking cows and working oxen. Teff straw is also used as mulch and is mixed with mud to build walls of houses, and of the grain storage facilities called *gotera* (Bultosa 2007). Recently teff straw (*Eragrostis tef*) was studied as a source of biosilica. In Ethiopia more than 2 million tons of teff straw is disposed-off as waste every year (Ayana Bekana Bageru 2018).

Most silica in commercial use is obtained from naturally occurring sources. Among the known polymorphs of silica, quartz and quartzite rocks are the most stable and relatively pure form that can be found in almost all mineralogical rocks and these mineralogical rocks are processed at high temperature to produce sodium silicate (C. Setzer 2002). Others sources of silica are tetraethoxysilane (TEOS), and tetramethoxysilane (TMOS). The mentioned sources are commonly used for the synthesis of silica particles. Due to their flammability, high cost, and difficulties in handling (transportation and storage), these are not promising sources of commercial silica (Ayana Bekana Bageru 2018).

Silica can be classified as crystalline and amorphous silica according to their structure. Crystalline silica represents a form of silica which is highly organized frame work pattern. Quartz is the most common crystalline form of silica encountered in nature. Crystalline silica is hazardous to human health and is classified as human carcinogen. But crystalline silica in the form of quartz is stable under most earth surface conditions, has very low solubility under a wide range of environmental conditions such as (PH, salinity and redox potential) thus tends to persist the environmental (RJ Southard 2014).

Amorphous silica does not have a crystalline structure as defined by x-ray diffraction measurements. Amorphous silica can be naturally occurring or synthetic. Synthetic amorphous silica can be broadly divided into two categories of stable materials called vitreous silica or glass and Microamorphous silica. Vitreous silica is made by fusing quartz at temperatures greater than approximately 1700^{o}C. Microamorphous silica includes silica sols, gels, powders, and porous glasses. These consist of ultimate particles of the inorganic polymer (SiO2)*n*, where a silicon atom is covalently bonded in a tetrahedral arrangement to four oxygen atoms (C. Setzer 2002).

There are different types of micromorphous amorphous silica processed from quartz and also its application differs as well. Some of them are silica sols or colloidal silica, silica gel and precipitated silica. Colloidal silica is a stable aqueous dispersion or sol of discrete amorphous silica particles having diameters of 1 to 100 nm. Silica sols do not gel or settle out of solution for at least several years of storage. Colloidal silica is used for making paper, floors, fibers, films and for clarifying wines and beers. Silica gel is a coherent, rigid, continuous three-dimensional network of spherical silica in which the pores are interconnected and filled with liquid. Silica gels are used as absorber and in cosmetics products. Precipitated silica is particles of colloidalsize silica that have not become linked in a massive gel network during the preparation process. Precipitate silica is used in detergents and cleaners as extenders, in rubber and tire fillers and in shoe sols (C. Setzer 2002).

Recently the sources of silica in biomass resources such as rice husk and wheat husk are being researched intensively for several industrial applications. Most biomass resources are waste by-products whose disposal causes environmental pollution. Hence using biomass resources for substituting renewable resources are the best choice for sustainable development. Currently silica is used for different applications. Some of them are for reinforcement of silicone rubber, as

adsorbent, for purification and stabilization of rubber, for cosmetics, for glass making, for production of thermal insulation material and also for paper industry (Bajirao S. Todkar 2016).

Nowadays teff straw is being researched for different purposes such as biomethane production (Akiber Chufo 2015), for heavy metal removal and bio silica production (Ayana Bekana Bageru 2018).

Generally, there are two conventional methods for manufacturing of reactive silica from biomass, called bio-silica, namely chemical and the thermal methods. In combustion method, the biomass directly gets decomposed thermally at high temperature in order to remove its carbonaceous content. Here the combustion can be direct combustion or combustion after pretreatment. Chemical method involves reaction of biomass with alkali or other chemicals, called as digestion, to extract silica in the form of sodium silicate. In chemical method the ash can react with sodium hydroxide (Ayana Bekana Bageru 2018), reaction with sodium carbonate , hydrogen fluoride (Sun 2001) or can be treated by hydrothermal method (N. Soltani 2014).

When the biomass reacts with sodium hydroxide to give sodium silicate and precipitates using acid solution it is called sol gel method. Different studies have been done using the sol gel method from different biomass. (Ayana Bekana Bageru 2018) reported that teff straw can be used for the preparation of bio silica using sol gel method. This method can be affected by different parameters during the process such as sodium hydroxide concentration, extraction time and extraction temperature. Detailed literature review shows that studies on the effect of process variables on the silica synthesis from teff (*Eragrostis tef*) straw via sol gel method are not reported. In the present work, therefore, silica has been synthesized from teff straw using sol gel method and the effects of process variables on the extraction of silica yield and its physiochemical properties such as composition, structural, and functional properties have been studied.

1.2. Statement of the problem

Even though Ethiopia is one of the richest countries in underground minerals like quartz, mining of this rock has long-term environmental impacts. Some of the negative impacts are disruption of the hydrological cycle, loss of biological diversity, acceleration off deforestation and desertification in fertile areas, destruction of cultural heritages, noise pollution and poor sustainable development for the future. The conventional industrial method of preparing silica is that sodium carbonate powder reacts with quartz sand at high temperature (1400^0C) to form sodium silicate, and then the obtained sodium silicate reacts with sulfuric acid in order to precipitate silica. This method was hazardous to the environment because of production of 0.23 ton carbon dioxide (CO_2), 0.74 ton sodium sulfate and 20 tons waste water during the preparation of 1 ton of silica by using 0.51 ton of sulfuric acid and 0.53 ton of sodium carbonate (N. Soltani 2014).

In recent years, one of the world's primary concerns is the "greenhouse" effect, especially relating with CO_2. The main disadvantages of the traditional technique are the high-energy consumption and the high levels of pollution. The processes produce large quantities of CO_2 and inorganic salts, which have limited their large-scale commercial applications and violated the principle of sustainable development. Other than the sodium silicate tetraethoxysilane (TEOS), and tetramethoxysilane (TMOS) are also the sources of silica. Due to their flammability, high cost, and difficulties in handling (transportation and storage), these are not promising sources of commercial silica. It is believed that a cheaper and environmental benign route to produce silica powder with desirable materials attracts much more attention.

Teff straw has no commercial value except for the use as animal fodder, open-burning, and mud-composite for house making in rural areas. More than 2 million tons of teff straw is disposed-off as waste every year (Ayana Bekana Bageru 2018).

There are two scientific researhes which has been done recently in converting teff straw in to bio-silica by Bageru and Serivista. However in those researches there is a gap in studying the optimization and effet of eah process parameters on the yield of silica.

Therefore to reduce the long term enviromental impact of mining quartz, to reeduce the air and water pollution, to meet the green production and gain commercial value the teff straw a large focus must be given on the utilization of teff straw for the production of bio silica.

1.3. Objective

1.3.1 General objective

The general objective of this research is extraction, characterization and optimization of silica production from teff straw by using alkali solution.

1.3.2 Specific objectives

- ✓ To characterize the raw teff straw and to determine the compositional analysis of teff straw ash after burning
- ✓ To characterize the extracted silica using FTIR spectroscopy analysis and XRD analysis
- ✓ To Optimize the process parameters of extraction of silica which are NaOH solution concentration, extraction time and extraction temperature for maximum production of silica (SiO_2)
- ✓ To study the removal efficiency of methyl orange solution using the extracted silica

1.4 Significance of the Study

This paper is an experimental study of alkali extraction method of silica from teff straw and it has a large significance in creating sustainable production process of silica in Ethiopia by substituting renewable source of silica (quartz) by nonrenewable source which is teff straw. Since the conventional process produces causes high level of water and air pollution, this production process reduces those problems. If this produced silica commercialized in large scale, it will eliminate or decrease the silica imported amount.

CHAPTER TWO

2. Literature Review

2.1. Sources of Silica

Conventional silica precursor is sodium silicate which is manufactured by expensive process of smelting quartz sand with sodium carbonate at 1300°C (Ayana Bekana Bageru 2017). This quartz is never found in its natural state and alloys with a number of different metals. Approximately 95% of silica is found in the form of crystalline form (N. Soltani 2014). Another silica precursor is Alkylorthosilicates such as polyethlydiorthosilicate, tetraethylortothosilicate and tetramethyleorthosilicate conventional precursor for synthesis of commercial silica in the presence of catalyst (Ayana Bekana Bageru 2017). However, these are toxic and expensive raw material hence not feasible from environmental and economic point of view (Ayana Bekana Bageru 2018).

Currently the sources of silica are being researched intensively from biomass for several industrial applications (K.V. Selvakumar 2014), (Bajirao S. Todkar 2016), (Santana Costa 2018), and others researched extraction of silica from rice husk. The extracted amount of silica is averagely from 80-90 %.

Wheat straw is another source of silica. Wheat straw has about 9 % silica. When the wheat straw is burned it contains about 90% silica from the ash (Anaam Saeed 2011).

Recently (Ayana Bekana Bageru 2017) studied a new source of silica from teff straw (*Eragrostis tef*). The amount of silica extracted from teff straw varied as the ashing temperature varies. It has been studied by two methods which are: thermal and sol gel method. But using sol gel method the optimum operating temperature is not studied (Ayana Bekana Bageru 2018).

2.2. Amorphous Silica

Amorphous silica (SO_2) is a type of silica that doesn't have a crystalline structure as defined by X-ray diffraction measurement. Amorphous silica can be naturally occurring or synthetic. It can be applied in different processes such as in coating, anti-blocking films, polymer filling, catalysis, adsorption etc. The functionality of amorphous silica is influenced by its structure, surface chemistry, pore size and macroscopic structure (C. Setzer 2002).

2.2.1. Types of amorphous silica

Synthetic amorphous silica can be classified in to four general classes. These are colloidal silica (silica sols), precipitated silica, silica gel and fumed silica. There are two silica processes. The first one is wet process. Silica sols, precipitated silica and silica gel are prepared by wet process. The second one is thermal process. Fumed silica is processed by using volatilized reactants. Colloidal silica is called the primary particle because it is the basic building units of silica gels and precipitated silica. The polymerization of silica has three stages.

- ✓ Polymerization of monomers to form small primary particles
- ✓ Growth of primary particles
- ✓ Aggregation or agglutination of the particles to form a gel or a precipitate

Stage two and three highly depends on the pH and the electrolyte content of the silicic acid solution (C. Setzer 2002).

When the PH is above 7 in the absence of salts the growth of colloidal particles occurs but their number decreases. This process results in the formation of silica sols. When the solution is acidic (in the presence of electrolytes) the colloidal particles form gels by aggregation. The final silica gel property highly depends on the post- treatment steps which are washing, aging and drying. If the silica solution is neutral or alkali a precipitate is formed. The properties of precipitated silica is highly affected by PH, temperature, solid concentration and process conditions such as addition rate of raw materials, shearing action application (C. Setzer 2002).

Fumed silica (pyrogenic silica) occurs in the gas phase at high temperature using flame. The common process nowadays is the flame-hydrolysis process. In this process the raw material which is silicon tetrachloride is mixed with dry air and hydrogen fed to burner and then hydrolyzed. The characteristics of fumed silica are affected by reagent concentration, flame temperature and residence time in the combustion chamber (C. Setzer 2002).

A. colloidal silica

Colloidal silica is a suspension of fine-sized silica particles in a liquid phase. Stable suspension is prepared at concentration particles exceeding 50% solids. The particle size of suspension is approximately from 5-150 nm in diameter. Particles significantly smaller than 5 nm are difficult to stabilize at high concentration, while particles much greater than 150 nm are subject to gravitational sedimentation. Silica sols do not gel or settle out of solution for at least several years of storage (C. Setzer 2002).

Colloidal silica is processed when alkali silicate solution is partially neutralized by acidification and the reactive silicate species allowed growing on to silica nuclei. Then the resulting suspension is concentrated and stabilized. The stability of silica sols depends on several factors. The PH value should be >7 to maintain enough negative charge on the silica particle surface to prevent aggregation (C. Setzer 2002).

B. Precipitated silica

Precipitated silica is made by acidification of sodium silicate in which the primary particles formed are coagulated in to clusters. For the reaction sulfuric acid is usually used also some other acids such as hydrochloric acid, organohalosilanes and carbon dioxide. Precipitation is carried out under alkali conditions. The choice of agitation, duration of precipitation, temperature, concentration, and pH vary the properties of the silica. Precipitated silica differs from silica gel on the basis of pore structure. Precipitated silica has macro porous pore structure whereas gels have micro porous structure. Silica is precipitated by adding acid to sodium silicate to reduce the pH value of the hot suspension to a pH value of 9-10. Precipitated silica is used as extenders for detergents and cleaners, reinforcement, in paper processing and others (C. Setzer 2002).

C. Silica gel

Silica gel, a porous solid amorphous form of hydrous silicon dioxide, has the nominal chemical formula of $SiO_2.xH_20$. It is constituted by randomly linked spheroidal polymerized silicate particles, the primary particles. The sol-gel process is the most studied and most documented route for preparing amorphous silica. The initial step of the hydrolysis of sodium silicate is the release of silicic acid according to the following reaction (the precipitation acid is sulfuric acid) (C. Setzer 2002).

$$Na_2SiO_3 + H_2O + H_2S0_4 \rightarrow Si(OH)_4 + Na_2S0_4$$

The characteristics of a silica gel prepared by the sol gel route are highly dependent on the size of the primary particles aggregated to the 3D network and therefore are highly influenced by the pH of the starting silica sol. Depending on the pH of the solution different charged species are formed. When the pH is less than 2, the protonated form ($(H0)_3SiOH_2^+$) is observed. When the pH is 7, the protonation of silanol groups occurs and results in the formation of an anionic species ($(HO_3)\ SiO^-$).The silicic acid quickly starts to polymerize by a condensation reaction, resulting in the formation of dimers, trimers and polymeric acid. Unlike organic polymer systems

that form branched and cross linked chains, Iler recognized three stages of polymerization (C. Setzer 2002).

1. Polymerization of monomers to form small primary particles,
2. Growth of primary particles,
3. Linking of particles into branched chains, networks and finally gel.

The polymerization of silicic acid involves an ionic mechanism in which the monomers must react with an ionized species. The polymerization reaction is highly pH dependent.

The rate of polymerization is slowest at pH ~ 2 because the point of zero charge and isoelectric point. The point of zero is the condition where the surface charge is zero and the isoelectric point is where the electrical mobility of the particle is zero. In this pH, the growth of the primary particles stops when their size reaches 2-4 nm (C. Setzer 2002).

$$(HO)_3SiOH + (HO)_3SiOH_2^+ \rightarrow (OH)_3Si\text{-}0\text{-}Si(OH)_3 + H_30^+$$

The gel time steadily decreases between pH = 2-6. It is assumed that the condensation occurs by a bimolecular nucleophilic mechanism.

$$(HO)_3SiO^- + (HO)_3SiOH \rightarrow (OH)_3Si\text{-}0\text{-}Si(OH)3 + OH^-$$

Above about pH = 7 the polymerization mechanism is different. This is caused by two effects:

1. The particle surfaces are highly charged, which makes particle aggregation unlikely
2. The solubility of silica is much higher, and the impact of the particle size on the solubility is more marked.

The growth of the primary particles continues by Ostwald ripening. Smaller, more soluble particles dissolve and reprecipitate on the surface of the larger, less-soluble ones. At room temperature, the particles grow to a size of 5-10 nm in diameter. In the presence of salts, chaining and aggregation occur, leading to the formation of a gel (C. Setzer 2002).

The surface area of an untreated silica gel is inversely proportional to the pH of the starting silica gel. Since the size of the primary particles that form the gel is proportional to the pH, the BET surface area is determined by the size of the primary particles. When the primary particles that form the gel are small, the surface area of silica becomes higher. In addition to the surface area, the pore volume of the raw gel is influenced by the pH during the sol-to-gel transition phase. Washing, aging time and drying also has an impact on the pore structure of silica gel (C. Setzer 2002).

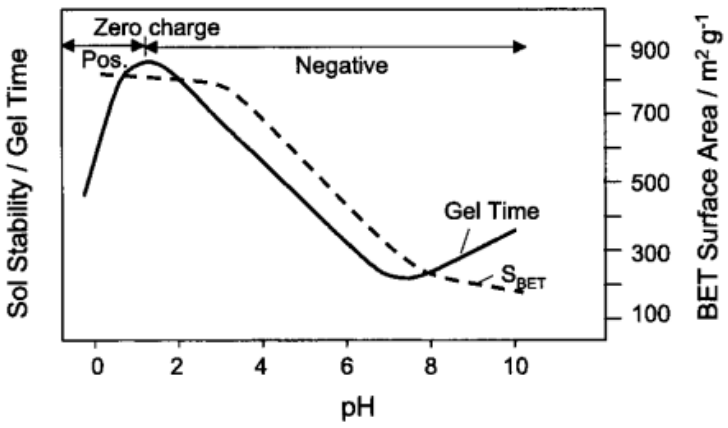


Figure 2. 1 The effect of pH on gel time and the BET surface area of a gel (C. Setzer 2002)

2.3. Application of Amorphous Silica

The silica gel is used in different applications such as:-

Cleaning, Polishing and Planarization- Amorphous silica particles are used as abrasives and cleaning agents in several applications. In dentifrice products both gels and precipitates are incorporated for the purposes of stain removal. These particles range in size from roughly 3 to 20 pm and, though porous, typically have a much lower pore volume than silica used for thickening applications. Additionally, silica dentifrice abrasive particles are usually reinforced by silica deposition during processing in order to further enhance their cleaning properties. Optimally prepared particles give good cleaning performance without scratching the enamel surface (C. Setzer 2002).

Adsorption- Silica gels are the most widely used amorphous silica adsorbents due primarily to the range of pore sizes with which they can be prepared. Amorphous silica subjected to moderate drying conditions typically has a silanol surface which is polar due to the electronic asymmetry of the oxygen and hydrogen atoms. This surface interacts strongly with both polar and readily polarizable species and will generally adsorb these species preferentially from mixtures with less polar compounds. In the presence of water, or other strongly polar solvents, the acidic silica surface has point charges that allow ionic interaction with charged molecules (C. Setzer 2002). Bio silica which is extracted from raw teff straw by thermal method was used for the adsorption of pyridine which is a harmful effluent chemical from industries. The adsorption efficiency of 71±2.8, 82±2.5 and 96±1.9% from silica obtained from ashing temperature of 500^0C, 700^0C and 900^0C respectively (Ayana Bekana Bageru 2017).

Matting Agents- Silica is used as a matting agent in lacquer or coating systems. Silica gels as well as precipitated, fumed and colloidal silica's are used for this purpose. The mechanism of matting by silica particles is that uniformly dispersed silica particles in the liquid-applied coating create a microrough film surface as the coating shrinks during drying. The nonplanar surface results in diffuse reflection of incident light and, hence, the matte effect (C. Setzer 2002).

Ink-receptive Coatings -The print quality of an ink-jet image is dependent upon the printer, ink and media. The media performance is affected by the binder, additives, and the active silica particle. Because of their porous structure, silica can provide a superior liquid uptake, which results in reduced dry times and improved print quality. The effective- of the silica particles depends on both the internal as well as external (inter- particle) porosity (N. Soltani 2014).

Antiblocking Agent- Silica is added to polymer film resins in order to prevent films from sticking together after their formation, or during further processing. Both precipitated and gel type materials are used in this application. The incorporation of silica particles in the polymer film creates a microrough surface (C. Setzer 2002).

Reinforcing Agent – silica is used as reinforcing filler is to improve critical mechanical properties of the rubber including tensile strength, tear and abrasion resistance. For these applications only precipitated silica is used and not gel based materials. One advantage of precipitated silica over carbon black in these markets is that the production of durable goods like shoe soles in colors other than black is possible. The degree of reinforcement increases roughly with increasing particle size. Another important reinforcement application is silicone rubber where precipitated silica has replaced fumed silica. This became possible because of adjusted product design for this application in terms of product purity and lower water adsorption (C. Setzer 2002). Silica prepared from rice husk by sol gel method was used as filler in rubber tire. In the conducted research they stated that the overall mechanical properties like hardness, young's modulus, abrasion resistance of rubber products reinforced with rice husk ash silica was better than commercial silica filled rubber composite (Addis Lemessa Jembere 2017).

Defoamer- the formation of stable foams can cause major problems in industrial processes such as in the manufacturing of paints and coatings, textiles, paper, detergents, and in the chemical industry. Here, foam can either affect the quality of the final product or impede the manufacturing process by reducing the capacity of tanks or containers or by causing pumping problems. For this reason, foam control processes have been developed. Highly effective foam

control systems, with no negative impact on the manufacturing process or final product, are dispersions made of oils and hydrophobic, pre-treated, silica with a great variety of silica being used. In addition to their use as highly effective active component in foam control systems, silica also finds use as anti-settling agent in the manufacture of defoamers thus stabilizing the defoamer system providing a longer shelf life and consistent quality (C. Setzer 2002).

2.4 Crystalline Silica

Crystalline silica represents a form of silica, which is in a highly organized, framework pattern, referred to as tectosilicates in the classification scheme of silicate minerals (stishovite is an exception and is often classified as an oxide rather than as a silicate). The term crystalline refers to the orientation of SiO_2 molecules in afixed pattern, as opposed to a more randommolecular arrangement defined as amorphous, noncrystalline, or short-range order. The oxygen and silicon atoms of silicon dioxide are arranged in a threedimensional pattern repeated in definitely in three directions, forming the crystalline structure. Each Si atom is bonded to four O_2atoms, and each O_2atom is bonded to two Si atoms. Quartz is the most common crystalline form of silica encountered in nature (RJ Southard 2014).

Most human exposure to crystalline silica occurs in the workplace, rather than in the general environment. Sandblasters, who use sand for cleaning surfaces, generate dust clouds of freshly fractured crystalline silica and are at greatest risk. Other occupations where exposure is common include mining or rock quarrying, where blasting and excavation activities may suspend dust containing crystalline silica, and farm laboring where mineral dusts are generated infield preparation. Crystalline silica in the form of quartz is stable under most earth surface conditions, has very low solubility under a wide range of environmental conditions (e.g., pH, salinity, and redox potential), and, thus, tends to persist in the environment. The main health risk regarding crystalline silica is via occupational exposure. Crystalline silica exposure may cause silicosis (a serious lung disease), cancer, and death (RJ Southard 2014).

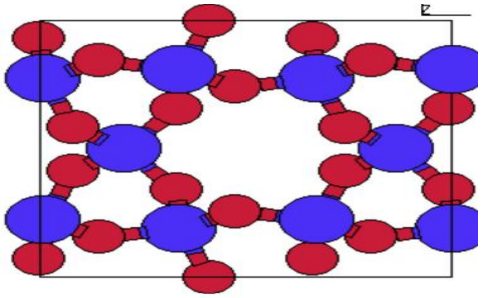


Figure 2. 2 structure of crystalline silica

2.5 Silica Production from Organic Waste

Bio silica is reactive silica extracted from various biomasses by different method and used for different applications. Bajirao et al introduces a simple process to manufacture precipitated silica from waste rice husk. They stated that extraction of silica from waste burned rice husk requires high extracting temperature (180ºC-200ºC) and pressure ranging from 6-8 atm. But high reaction temperature and pressure can be avoided if ash obtained by burning rice husk at 650ºC is used. This ash is mostly amorphous silica which is reactive around 100ºC with NaOH solution at atmospheric pressure to yield sodium silicate. The precipitator used was sulphuric acid and said that the addition of the acid should be very slowly otherwise the chemistry of such mass may change along with physical properties (Bajirao S. Todkar 2016).

Another researchers investigated the effect of washing rice husk ash with different acids (HCl, HNO_3 and H_2SO_4) prior to alkali extraction, the degree of agglomeration and yield of silica. In the above study they stated that the degree of agglomeration was investigated by using SEM (Scaning electron microscope). The agglomeration and yield was high when HCl acid was used for pretreatment. The amount of moisture content on the extracted silica was low when the rice husk ash was pretreated when acid (K.V. Selvakumar 2014).

The parameters such as calcination time and temperature for obtaining the rice husk ash, and the extractor concentration and reaction time were evaluated by Jose (2018) for the extraction of amorphous silica. The raw rice husk ash was rinsed with deionized water to remove the unwanted materials and dried in oven 60^0C for 24 h, grounded and sieved (48) mesh. Then 50 g of each variety of ground rice husks was placed under magnetic agitation in 500 mL of a solution of 3 mol/L HCl at room temperature for 24 h, in order to remove impurities. Subsequently, the mixture was filtered under vacuum with deionized water until a constant pH was achieved and then it was dried in an oven at 60^0C for 24 h. The amorphous silica was extracted from the rice

husk ash by sodium hydroxide solution with a ratio of 10 mL of solution for each 1 g of rice husk ash under heating and intensive stirring. The sodium silicate solution was precipitated by treatment with a solution of sulfuric acid. The obtained result was about 98% pure and dominantly amorphous silica was obtained from treated rice husk ash. He suggested that the best extraction and yield results were obtained in the design using a concentration of 4 mol/L of NaOH and reaction time of 4 h with a yield of about 98.30% pure silica (Santana Costa 2018).

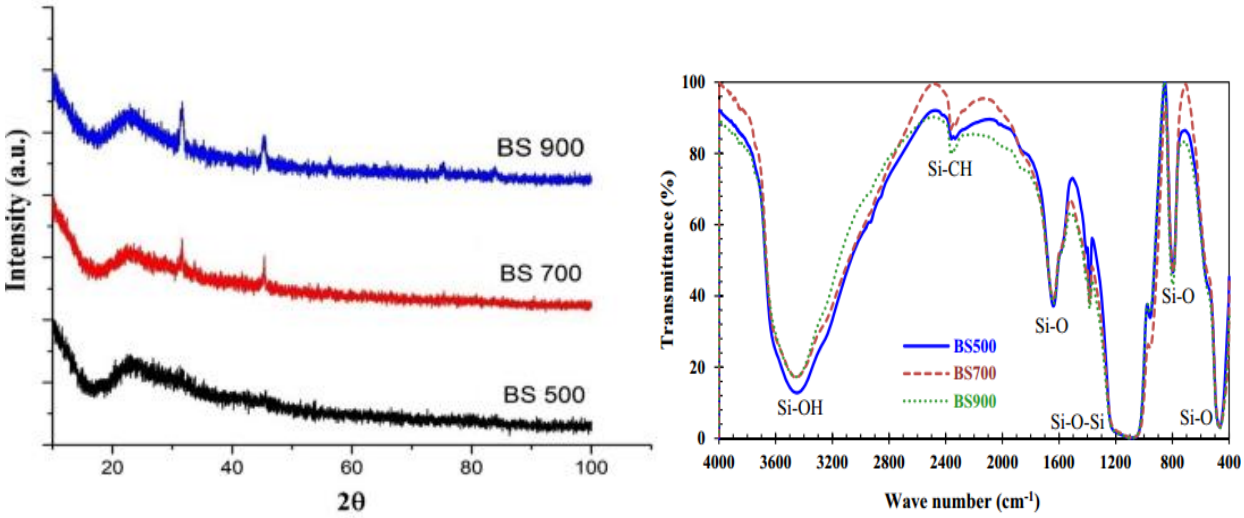
(Ikram Ul Haq 2014) made attempts made to extract silica from the rice husk ash by directly extracting the rice husk ash without acid pretreatment. The author extracted silica with sodium hydroxide concentration of (0.2-1.2 mol/L) and heated with reflux condition for various periods of times (20-120 min) and the dispersion was filtered with filter paper and the liquid part was precipitated with sulfuric acid. He studied the effect of experimental parameters and suggested that the amount of silica is optimum when the sodium hydroxide concentration is in the range of 0.8-1 mol/l and 90 minutes of extraction time.

(Khushbu G. Patel 2016) produced silica gel from agricultural waste which is wheat straw. Alkaline-solubilization and acid-neutralization method was used to obtain gel from silica obtained from wheat straw. Wheat straw was treated with hydrochloric acid in a microwave digester. Acid treated product after removal of excess acid was calcined at 550°C. Fine white powder was obtained after calcination. The silica gel was obtained by treating 1g of the ash with 100ml of 1N NaOH solution. Mixture was refluxed for 1hr with constant stirring. The sodium silicate solution was filtered and the liquid part was precipitated with 1 N HCl. The silica gel obtained from wheat straw was used for a nitration reaction without using nitric acid as a catalyst.

The optimum conditions under which precipitated silica can be obtained was studied by (Anaam Saeed 2011). Wheat husk was calcined in electric tube furnace at 500^0C for two hours to produce wheat husk ash. The wheat husk ash was treated against sodium hydroxide at different molar ratios and reaction time to obtain sodium metasilicate. Each time sodium metasilicate was treated against 0.1N HCl to recover silica in precipitated form. Under the experimental condition the obtained optimum Na/Si ratio was 2 with pure silica conversion of 90.5%. It has been observed that one hour boiling of the mixture is optimum to obtain sodium silicate.

(Ayana Bekana Bageru 2017) produced silica from teff straw by thermal method. The teff straw was pretreated by hydrochloric acid subjected to thermal decomposition. The thermal

decomposition was done in an electric muffle furnace and the ashing temperature was 500^0C, 700^0C and 900^0C for 2 hours. The Prepared teff straw ash had a considerable amount of silica with a percentage of 84.9 %, 91.2% and 91.81% for ashing temperature of 500^0C, 700^0C and 900^0C respectively. The same researchers again prepared bio silica from teff straw using sol gel method. In this study the teff straw was leached using HCl solution with a reflux setup at 80°C for one hour. Then the pretreated teff straw was neutralize with deionized water until the pH becomes neutral and then dried in hot air oven. The dried teff starw was calicined in a muffle furnace at temperature of 500^0C, 700^0C and 900^0C for 2 hours and then the prepared ash was extracted using 2.5 N NaOH. The next step was gelification process and filtered. The sodium silicate solution was gelified by adding HCl acid drop wise and aged for 20 hrs. The prepared gel was washed to remove the soluble salt and dried. The authors stated that 99 % pure bio silica was obtained from teff straw ash prepared at 900^0C. The XRD and FTIR test results of the bio silica from teff straw of the above study are displayed below (Ayana Bekana Bageru 2018).



(A) (B)

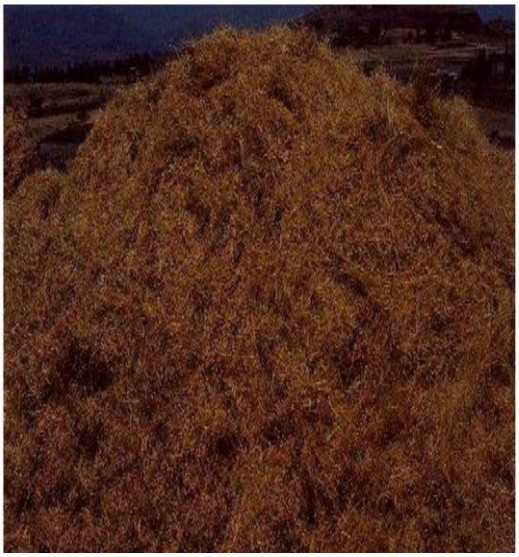
Figure 2. 3 (A) X-ray diffraction (XRD) spectra of synthesized biosilica samples (B) FTIR spectra of synthesized biosilica samples. (Bageru and Srivastava 2018)

2.6 Teff *(Eragrostis tef)* and Teff Straw

Teff is a C_4 self-pollinated tetraploid cereal plant with a chromosome number of 2n=4x=40. Teff is also an allotetraploid plant. In most varieties the plant height is 50–120 cm. A single teff plant is known to produce from 9000 to 90 000 grains depending upon the variety and production conditions. Tef, Eragrostis teff is a staple food crop in Ethiopia and Eritrea. It belongs to the

family Poaceae, subfamily Eragrostoideae, Tribe Eragrostae and genus Eragrostis. The genus contains about 300 species. The recorded history of Ethiopia explained that the pre-semitic inhabitants domesticated teff in between 4000 and 1000 BCE. Its grain is mainly used for making different kinds of Enjera (pancake-like flat bread), porridge and feed. It is also used in making a local alcoholic drink called Arak'e or katikalla and a native beer called T'ella or Fersso. Recently teff started to be produced in United States for for the health-food market, In South Africa, teff is widely grown as a fodder crop during the summer-rainfall season. In Australia, India, Kenya, and the United States, it is cultivated as a forage crop. The straw is used mainly for reinforcing mud for plastering wooden walls of buildings and for livestock feed. It is also used as mulch (Bultosa 2007). Teff straw has no commercial value and More than 2 million tons of teff straw is disposed-off as waste every year. Recently some researchers have shown an interest for various applications such as preparation of activated carbon for removal of heavy metals like chromium from tannery wastewater and bio methane production (Akiber Chufo 2015; A.B. Wassie 2016). The straw to grain ratio is 2:1. (Addis Lemessa Jembere 2017)Ethiopia produced 52, 834,011.56 quintal of teff in 2018 GC (Egency 2018). Therefore the amount of straw produced was 105,668,023.12 quintal in 2018. Teff straw has about 52% of silica (Abrham Bayeh Wassie 2017)





(A) (B)

Figure 2. 4 (A) teff pant (B) mass of teff straw (Refera 2001)

Table 2. 1 XRF result of teff straw (Abrham Bayeh Wassie 2017)

Constituents	Constituents in %
MgO	1.9775
Al_2O_3	1.5461
SiO_2	52.2263
P_2O_5	3.9219
SO_3	4.1058
Cl	0..3775
K_2O	3.9259
CaO	17.6622
TiO_2	0.6871
Cr_2O_3	0.8198
MnO	2..3899
Fe_2O_3	9.7397
CuO	0.1833
ZnO	0.3512
SrO	0.0858

The above XRF result from the literature shows that there is a huge amount of silica in the straw and favors silica production.

2.7 Surface Chemistry of Amorphous Silica

Amorphous silica does not have a crystalline structure as defined by X-Ray diffraction measurements. Silica is a useful chemical with a chemical formula of SiO_2.each Si atom is surrounded by four O atoms and O atom serves as a neighbor to two Si atoms there by leading to a condensation product with a formula SiO_2.Silica occurs in nature mainly in three crystalline fours namely quartz (hexagonal), cristobolite (white) and tridymite (hexagonal) and also in amorphous form like opal. Amorphous silica bears silanol groups on the surface as well as exposed siloxane (Si-0-Si) bonds. There are three kinds of silanol groups on the surface: isolated, geminal, and vicinal. An isolated silanol group is an OH group located on a Q^3 silicon site that is not hydrogen bonded. In Q terminology, the superscript (0-4) is the number of bridging oxygen atoms surrounding the central Si site. Vicinal diols are hydroxyl groups located on neighboring Q^3 sites and which are close enough to form a hydrogen bond. Geminal silanols are defined as two OH groups located on Q^2 silicon sites that are too close to form a hydrogen bond between each other. The surface also contains exposed siloxane bonds (Si-0-Si) (C. Setzer 2002).

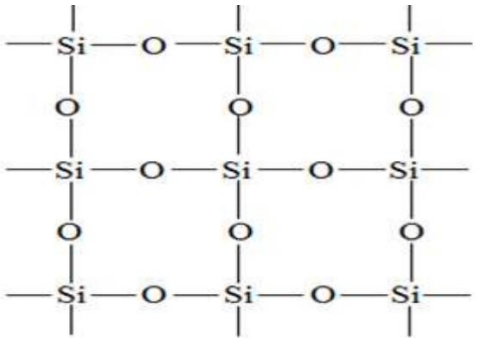


Figure 2. 5 Structure of Amorphous Silica (C. Setzer 2002)

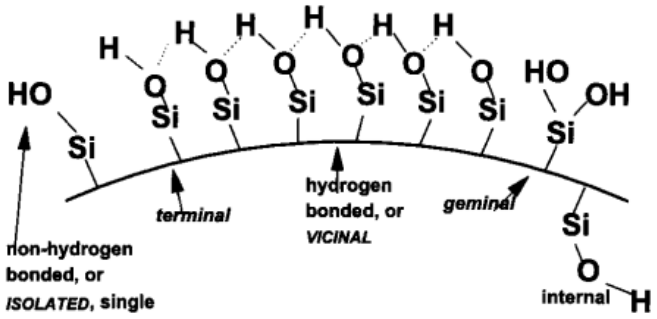
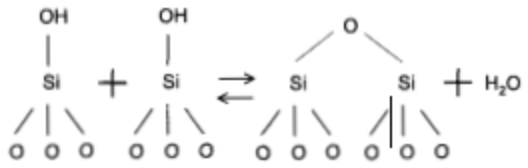


Figure 2. 6 Types of Silanol Groups (C. Setzer 2002)

Infrared spectroscopy has been widely applied when studying the silica surface. The region 1950-1766 cm^{-1} is attributed to an overtone structure vibration. Because it remains unaffected by different treatments, its integrated value is used as a reference band to normalize all other intensities. The vibrations at 3730-3720 cm^{-1} and 3250 cm^{-1} have been assigned to the interaction of the oxygen of the hydroxyl group with the hydrogen of the neighboring hydroxyl group. The table below summarizes the best accepted infrared attribution. Silanols present on the silica surface can be thermally removed with formation of the siloxane bond and release of water molecules. This can reduce the amount of water or OH bond on the silica and the amount of vibration on the infrared band (C. Setzer 2002).

Table 2. 2 Infrared band assignments of silica

Silanol Type	*IR absorption band/position (cm^{-1})*
Nonhydrogen bonded	3740
Terminal Si–OH	3720–3680
Geminal	3700–3600
H-bonded, internal	3670–3640
H-bonded, external	3540–3520
Trapped water	3400–3100



Equation 2.1 Thermal dehydroxylation (C. Setzer 2002)

Amorphous silica is distinguished by chemical composition, physical properties, and characteristics of the particles. Exact analytical procedures depend on the type and intended application of the amorphous silica. The most important chemical information is the amount of silica, % SiO_2 (Othmer 2007).

2.8 Silica Processing Methods

2.8.1 Conventional Silica Processing Method

The conventional preparation of silica is reacting quartz sand with soda in suitable furnaces at temperature range from 1400^0C-1500^0C to form sodium silicate or silica glass. The melt which solidifies on cooling ("solid glass") is dissolved in water under pressure at elevated temperature in another process step and the solution obtained is optionally filtered, depending on the quality requirements and the obtained sodium silicate reacts with sulfuric acid to precipitate the silica. However, this high temperature fusion process is very expensive both in terms of apparatus and in terms of energy consumption and, in addition, it can produce considerable air pollution by emissions such as dust, nitrogen oxides, and sulfur oxides. In production of 1 ton of silica 0.23 ton of carbon dioxide, 0.74 ton of sodium sulfate and 20 tons of waste water is emitted to the environment. This traditional method consumes high energy and emitted high levels of pollution to the environment (N. Soltani 2014).

2.8.2 Silica Processing Methods from Biomass

1. Direct combustion

The biomass can be directly combusted to produce silica without any pretreatment. In the reaction process the phase combusition of silica in the ash and its surface area depend critically on thee combusition temperature of the raw material. The other factors that affect the quality of silica produced are the combustion instrument, ashing temperature and heating rate (Sun 2001).

2. Combustion after pretreatment

The acid solutions used for pretreatment of the raw material are HCl, H_2SO_4, HNO_3 and HF. Acid treatment of RHs prior to combustion does not affect the structural nature (amorphicity) of the silica produced. Some alkalis,such as NaOH and NH_4OH, have also been used to pretreat the biomass However, the effects of alkali pretreatment are not as obvious as the effects of acid pretreatments. Microbial fermentation has also been applied to pretreat RHs at low temperatures to release silica in its natural, pure and highly reactive form. Such microbiological processes are relatively cheap, and if used in combination with acid leaching, it can result in the production from RHs of silica that is similar to a commercial xerogel. Its purity, specific surface area, and tendency to form fractural structures resemble the features of fumed silica. Its disadvantage is the pretreatment requires high processing time. After pretreatment the biomass is combusted in furnace and produces white silica. (Sun 2001) Bageru and Srivastava use HCl acid for pretreatment and the produced silica was white and 84-91 % pure (Ayana Bekana Bageru 2017).

3. Hydrothermal Method

Hydrothermal production process is leaching process which requires high-temperature (T>243°C), high-pressure (P>3MPa) and acidic media with strong oxidation activities. The organic compounds can be decomposed, and the trace metals can be turned into soluble ions then silica can be obtained. The theory behind the process is that water as a sole aqueous medium, can be dissociated at high temperatures and pressures, forming hydronium (hydrated proton or protonized water) ($H3O^+$) ion as well as the hydroxyl (OH^-) ion. Thus, this acid-base system is capable of reacting with basic and acidic oxides as well as the organic components (the hemicellulose, cellulose and lignin). Except for phosphorous oxide that tends to remain in the solid phase in large quantities, most of the impurities existing in the biomass can be removed after 30 minutes (N. Soltani 2014).

In this method, the reaction temperature is much lower than that used in the combustion method, and it is easy to retain the amorphicity of the extracted silica. Some acids with strong oxidation activities such as $H_2SO_4$and HNO_3 are used; sometimes H_2O_2 is also used as the oxidative medium. However this process is complicated and needs instruments which are sophisticated (Sun 2001).

4. Reaction with Sodium carbonate

When the biomass is prepared in ash form it reacted with Na_2CO_3 solution in the proper ratio for 3 hours. After the product was washed, filtered, dried, and ground, silica with acceptable purity was obtained. Temperature has high effect on the product. When the temperature is low, the purity of the silica becomes low and whereas when the temperature is low the yield and quality of the silica becomes low. The proper reaction temperature and time are 600-650 °C and more than 3.5 h respectively. This production process requires high temperature and reaction time than the other production processes (Sun 2001).

5. Reaction with hydrogen fluoride

One of the chemicals which can be used to extract silica from its ash is hydrogen fluoride. The ash is reacted with hydrofluoric acid to give H_2SiF_6 to this ammonia is added to give a complex $(NH_4)_2SiF_6$ and decomposes into NH_4F and SiO_2. The filtrate is reacted with strong acid to give HF which is recycled. Since HF highly corrosive it is disadvantageous and the organic constituent is not utilized (Sun 2001).

6. Reaction with Sodium Hydroxide

In this method the first stage is producing the ash by combustion of the selected biomass. Then the produced ash is mixed with NaOH to produce sodium silicate solution. Then, the sodium silicate was reacted with either NH_4HCO_3, $(NH_4)_2SO_4$, H_2SO_4 or HCl to produce silica. The proper concentration of NaOH and mixing speed are also important. When the produced sodium silicate is titrated with acid, the silica gel can be precipitated when pH falls less than 10. (Ikram Ul Haq 2014) Several authors produce silica gel by this method and produce bio silica which has 99% purity (Ayana Bekana Bageru 2018).

The reaction was

$4NaOH + nSiO_2(ash) \rightarrow H_2O + 2Na_2O.nSiO_2$

Addition of HCl causes silica precipitation

$2\ HCl + 2\ Na_2O.nSiO_2 \rightarrow 2\ NaCl + H_2O + n\ SiO_2\ (S)$

2.9 Thermal Treatment Technologies

The thermal treatment stage is one of the important stages in producing silica from the selected biomass. The widely used thermal treatment technologies to produce amorphous siliceous ash from biomass are the muffle furnace, the rotary kiln and the stepped grate furnace.

Muffle furnace

The major disadvantages of this method for thermal treatment of the biomass are high energy consumption (electrical power), batch-like process, and absence of mixing amongst the reactants, low production rate, long reaction time and risk of explosion. To maintain the temperature in the range of 600-700º C for the conversion process to take place, substantial heat needs to be supplied through electrical heating. There is no mixing between the reactants (the biomass used and oxygen) to increase the rates of mass and heat transfer, and therefore the biomass feed has to be spread as a very thin layer inside the furnace to ensure sufficient oxygen transfer on a micro-level (N. Soltani 2014).

Rotary kiln

When the biomass is used as a heat resource, it is necessary to blow air to achieve the highest possible combustion temperature. However, almost all of the biomass ash obtained by such procedure is crystalline and very low chemically active. It therefore has few practical uses. Rotary kiln consist of chimney which is erected on the hollow platform in communication with the interior of the hollow platform; a cone of biomass is formed around the chimney to completely cover the hollow platform. The inserted biomass at the small holes is ignited for smolderingly incinerating the biomass into carbonized biomass and the latter is allowed to self-burn into ash. In the continuous method for producing active Silica ash, downstream and upstream rotary kilns are connected in tandem; heating of the upstream rotary kiln is controlled to a temperature for burning biomass into ash. The biomass is supplied to the upstream rotary kiln to be smolderingly incinerated into carbonized biomass, then the carbonized biomass is supplied to downstream rotary kiln to be burned into ash, and finally, the resulting active ash is discharged from the downstream rotary kiln. In summary, since this procedure first carbonizes the selected biomass by burning it in an incineration furnace without flaming and then burns the carbonized biomass into ash, it enables easy production of white ash exhibiting excellent chemical reactivity (N. Soltani 2014).

Its major disadvantages, some of which are similar to those of the muffle furnace, are as follows.

- ✓ It requires temperature of at least 850º C (typically 1000º C) to achieve self-sustainable combustion.

- ✓ Combustion at temperatures less than 700º C (to prevent crystallization of ash) needs to be sustained by auxiliary fuel.
- ✓ High possibility of runaway reaction during char combustion stage.
- ✓ Long residence time.
- ✓ High energy consumption and
- ✓ Inferior mixing and possibility of hot-spot formation (N. Soltani 2014).

Inclined grate furnace

Inclined grate furnace is one of the available furnace types in which ash can be produced. Inclined grate furnace consists of a hull-feeding component, a combustion chamber, and an ash precipitation chamber. It is simple in construction and operation. The air for combustion is supplied by the suction of the dryer fan, while the fuel supply is facilitated by the vibration of a feeder connected by a wire to the fan shaft. However, it has incomplete combustion and inefficient ash separation so that ash and sparks are partially sucked by the fan into the dryer plenum. Despite of similar performance of inclined grate furnace to flat-bed dryers, the former has more durable steel parts than the later, particularly the grate, which is made of mild steel. One disadvantage of this technology is the non-uniformity in fuel-to-air ratio due to the non-uniform loading of biomass into the furnace. This leads to a significant amount of unburned carbon in the ash and a considerable loss in efficiency (N. Soltani 2014).

Fluidized bed process

A simple fluidized-bed reactor consists of a chamber containing a bed of inert particles such as sand, supported by a distributor plate. Pressurized air is passed through the distributor plate and the velocity of the air is progressively increased to support the entire weight of the bed by the fluid drag on the bed particles due to the upward flowing air. The bed is then said to be incipiently fluidized, and it exhibits fluid-like properties above this particular velocity, called minimum fluidization velocity. Because of being exothermic reaction with high calorific value, the external heating is required only during the start-up of the combustion of rice husk; the process is later self-sustaining (autogenous). The process can be operated continuously for large-scale operation. When the biomass combusted in the fluidizes bed it is easily removed from the fluidized bed by entrainment in the gas stream, from which it can be separated by a simple particle separating system such as cyclone. The control of critical process parameters,

such as temperature and residence time is achieved through the control of the ratio of air and rice husk feed in the fluidization chamber. The main advantage of the process is its flexibility to produce biomass ash of different grades (level of carbon content) depending upon the market demand (N. Soltani 2014). Some of the advantages and disadvantages of fluidized bed reactor are:-

- ✓ Continuous and self-sustainable combustion
- ✓ High combustion intensity
- ✓ Better ash composition and no ash sintering or ash removal problem
- ✓ Lower operating temperature range
- ✓ Optimum opportunities for temperature control
- ✓ Easier ash removal, no clinker formation
- ✓ Less excess air, higher CO2in flue gas
- ✓ Simple operation, quick start-up
- ✓ Fast response to load fluctuations (N. Soltani 2014)

2.10 Parameters affecting Silica Production from Teff Straw

In production of silica from teff straw there are a lot of factors that affect the yield and quality of the product which is amorphous silica.

2.10.1 Burning Temperature

The first factor is the burning temperature and burning time. When the combustion temperature of the biomass is too low, unburned carbonaceous materials is left with the ash and Burning temperature is too high it affects the structure of the silica and brings crystalline structure. It has been found that some kinds of metal oxides especially potassium oxide contained in ash cause the surface melting of SiO_2 particles and accelerate the crystallization of amorphous SiO_2 into cristobalite and tridymite. Moreover alkali metal impurities cause the remained carbons in ashes, originated in organics, after burning rice husk. This is because the eutectic reaction between alkali metals and SiO_2 element occurs during burning, and the carbon remains in the melt $SiO_2$and causes the crystallization of ash at lower temperature (N. Soltani 2014).

Burning the teff straw up to 700^0C gives amorphous silica while burning beyond 700^0C changes the form of the silica to crystalline structure (Ayana Bekana Bageru 2018). According to

(Anaam Saeed 2011) temperatures below 700^0C contribute to the presence of residual carbon and temperatures above 700^0C contribute to the formation of non-reactive crystalline silica.

2.10.2 NaOH Concentration and Extraction Time

In the silica production process digestion of the biomass ash with NaOH solution is an important step and it is called digestion step. Silica in the ash is soluble in sodium hydroxide solution and produces sodium silicate solution. The concentration of sodium hydroxide solution affects the yield of silica. Extracted silica gel from wheat husk at various Na to wheat husk ash ratios and different boiling time was studied by (Anaam Saeed 2011) . In their study they stated that maximum yield of silica was obtained at 2 Na/Si ratio and at boiling of 60 minutes. But at temperatures less than 60 minutes such as 30 minutes the yield of silica was small. In another research the effect of NaOH solution as extractor and extraction time from rice husk was studied by keeping the extraction time constant which is 90 minutes. The result showed that at concentration below 0.8 M of NaOH solution the yield of silica was negligible and above 0.8 M NaOH solution the yield increases gradually. In another part by keeping the NaOH solution constant which is 1M, the effect of extraction time was studied. They stated that at 30 minutes extraction time the yield of silica was very small and the yield increases gradually when the extraction time reaches 60 minutes. However, beyond 90minutes the silica yield became almost constant. (Ikram Ul Haq 2014) From these above researches the concentration of NaOH solution as extractor and extraction time has high effect on the yield of silica. No studies have been made on the optimization the yield of silica from teff straw.

(Santana Costa 2018) compared the yield silica from treated and untreated rice husk treated and untreated rice husk. The leaching chemical used was 3M HCl acid solution at room temperature for 24 hours and produces silica by sol-gel method. The yield of silica from treated rice husk showed an increase of 12% from the untreated rice husk also contributed to the production of a white rice husk ash. Another group of researchers stated that the leaching of rice husk by sulfuric acid prior to calcination removes 90% of the initial metal impurities such as K, Fe and Mn. (Rosario Madrid 2012) Another Researchers reported that leaching of rice husk prior to thermal decomposition increses the BET surface area and pore volume of acid-leached silica are higher than un-leached silica. This specifies that acid leaching produce significant effect on the surface area as well as pore volume of silica. The increase in surface area of acid-leached silica is mainly attributed to the hydrolysis of hemicellulose and cellulose into smaller compounds which could

decompose easier during combustion. They reported that acid leaching increases the silica purity and they compared that hydro chloric acid leached rice husk has an increase in 0.5% yield than the yield from sulfuric acid leached rice husk (Rohani Abu Bakar 2016).

(K.V. Selvakumar 2014) Studied the effect of different acids (HCl, HNO_3 and H_2SO_4) as a leaching chemical on the size and degree of agglomeration of the silica particles properties of silica from rice husk. They reported that high degree of agglomeration, high yield of silica which (85%) and completely white in color when the rice husk was treated by hydrochloric acid. In general they confirmed acid leaching increases the yield and decreases the moisture content of the silica from rice husk ash.

The acid leaching process decreases the degree of crystallization due to eliminating the impurities in the ash, resulting in higher purity of silica with a porous structure (N. Soltani 2014).

2.10.3 The pH of Precipitator Acid

The pH of the precipitator has a high effect on the gelation process. At pH 3, solid starts to precipitate, whereas gel formation is low. Silica yields gradually increase with increasing pH, with a maximum yield occurring at around pH 7. When the pH is greater than 8, formed gels are unstable and partially redissolved. At pH 11, these gels dissolve almost entirely in water. On the other hand, gelation pH has a great effect on porosity and particle size of produced silica. When pH increases from 3 to 7, particle size and porosity increases. The gelation process occurs due to polycondensation reaction (N. Soltani 2014).

2.10.4 The Aging Time

After the gel has first set, the degree of primary particle linkage is still relatively low. Only about 50 % of the particles are linked together. At that point, the gel is very soft. When the gel is kept in contact with its pore-filling liquid, it undergoes continuous change in properties and structure. This process is called aging. The aging at ambient pressure or under hydrothermal conditions leads to an increase in the average pore diameter and a strengthening of the gel matrix (C. Setzer 2002).

The drying temperature - The drying process leads to the formation of a xerogel. The drying conditions have a high impact on the structure of the final gel. The drying rate also affects the gel-network shrinkage. Fast drying results in less marked shrinkage than slow drying (C. Setzer 2002).

CHAPTER THREE

3. Materials and Methods

3.1 Materials

3.1.1 Raw Materials

The main raw material used for bio-silica preparation was brown teff straw. The brown teff straw has been selected because it is the highly cultivated type of teff than white and black teff in most parts of Ethiopia.

3.1.2 Chemicals

The chemicals used to prepare bio silica were:-

- ✓ Sodium hydroxide
- ✓ Hydrochloric acid (37%)
- ✓ Distilled water
- ✓ Methylene orange

3.1.3 Equipment

The lab equipment's used in this study are mentioned below:-

- ✓ muffle furnace
- ✓ Sieve analysis
- ✓ beaker
- ✓ hot plate
- ✓ crucible
- ✓ flask
- ✓ balance
- ✓ PH meter
- ✓ Dryer (oven dryer)
- ✓ Material handling (plastic bag)
- ✓ Grinder machine
- ✓ Electronic beam balance
- ✓ Mortal
- ✓ Filter cloth

3.2 Methods

3.2.1 Sample collection

Teff straw is highly available in most parts of Ethiopia. Brown teff straw were collected from Tuludimtu, Oromia, Ethiopia and transported to Addis Ababa Institute of technology. This research has been carried out in the laboratories of School of Chemical and Bio Engineering.

3.2.2 Raw Material Analysis

3.2.2.1 Moisture Content of teff straw

The moisture content of raw teff straw were determined as follows

The quantity of the raw teff straw retained below 2mm and weighed 5 gram. The prepared teff straw was dried in oven at a temperature of 105^0C until a constant mass was obtained. The experiment was replicated three times.

$$\mathrm{MC}(\%) = \frac{\mathrm{A}-\mathrm{C}}{\mathrm{C}} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \textit{Equation 3.1}$$

Where MC- moisture content of raw teff straw

A-Weight of teff straw in its natural state

C- Weight of oven dried sample

3.2.2.2 Determination of Ash Content

Ash content was determined using the VF2 model of muffle furnace. A 3gm of teff straw sample placed in a pre-weighted crucible is incinerated in a muffle furnace at 900°C until a complete ashing was achieved. The crucible is then transferred into a desiccator for cooling. Three replicate was made and the mass was measured used with a model of FA2004. The ash content was calculated by using the equation below

$$\text{Ash content of TS} = \frac{W_2 - W_0}{W_1 - W_0} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \textit{Equation 3.2}$$

Where, W_0 = the weight of the crucible,

W_1 = the weight of the crucible + sample before thermal decomposition

W_2 = the weight of the crucible + sample after thermal decomposition

3.2.3 Sample Preparation

As the teff straw is a bio mass of teff a lot of impurities could be mixed with it. In order to enhance extraction rate and purity of bio-silica in the down processes the sample needed to be pretreated.

1. Cleaning, soaking and washing

The sample was hand sorted physically and removes large size impurities such as leaves, sand, soil and non-teff straw grasses. Then the teff straw was soaked in tap water over night. In the next day the socked teff straw was washed 5 times to remove soluble impurities.



Figure 3. 1 Soaking of Teff Straw in Tap Water

2. Drying, Grinding and sieving

The washed teff straw was sun dried for 2 days to remove the moisture absorbed for the ease of grinding. The next process was grinding the dried teff straw using grinding machine and sieved by sieve analysis with 2.0 and 1.0 mm mesh opening and the particles size were below 2mm. The sample was grounded for ease of thermal treatment and maximum bio-silica recovery.



Figure 3. 2 Sun Drying of Washed Teff Straw

3. Acid leaching

The teff straw has alkali, alkali earth and transition metal impurities such as K, Na, Ca, Mg, Al, Fe, etc. Those metals can deposit in the cell or they can bind to the lignin or hemicellulose. To remove those metals acid leaching is important.The removal of the trace metals increases the straw surface area. Also, because of the removal of ionically bound metals from lignin or hemicellulose, chemical activation of carbonaceous content also occurs. This helps in removal of both organic and carbonaceous matter during high temperature ashing process. Overall, these impurities, if not avoided at early stage, might affect the final product's (silica gel) important properties such as porosity, color and specific surface area. The grounded teff straw was treated with 2.5 N analytical grade of HCl (36.46%). 50 gram of teff straw was measured using digital mass balance with a model of FA2004 and placed in 1000 ml beaker and 500 ml solution of HCl was added in the beaker. The prepared solution was heated with a hot plate a model of MH2lt for 1 hour at 80°C and stirred at 500 RPM with Euro-ST40D5000 agitator. The trace metals were soluble at the prepared HCl solution. The process was batch stirred lab scaled beaker which was agitated with coaxial impellers. The main function of the agitator was suppling unexhausted solvent to the teff straw. The volume of the HCl solution was enough in creating large surface area per unit volume. Since the teff straw could settle during the process an intensive stirring (500 rpm) was required to prevent this problem.



Figure 3. 3 Acid Leaching

4. Cooling, filtering, washing and drying

The leached solution was allowed to cool to room temperature naturally. Then a filter cloth was used for separation of acid leached teff straw from waste water. The filtered solid was further washes with water until the water pH becomes neutral. The washed sample was dried in oven over night at a temperature of 105 °C.



Figure 3. 4 Washed and Filtered Teff Straw

3.2.4 Teff Straw Ash Preparation

The pretreated teff straw was filled in 10 crucibles and placed in a muffle furnace with a model No of VF2. The temperature was set at 700 °C and calcined for 2 hours. The sample was subjected to thermal decomposition process. The selected temperature and time is enough time for obtaining constant mass of samples and also good enough to produce amorphous bio silica. Then after calcination the crucibles was placed in desiccator using a tong for cooling and also for absorbance of the atmospheric temperature. Then the ash was placed in air tight polyethylene

bag. The aim of this step is to increase the relative amount of silicon oxide by reduction of carbonaceous materials present in the samples, as well as to burn out other undesirable components detected by chemical analysis.





(A) (B)

Figure3. 5 (A) Ashing process in muffle furnace (B) Calicined teff straw ash

3.2.5 Bio Silica Extraction

Before proceeding to the extraction process, different NaOH concentration solution was prepared. The molarity of NaOH solution was calculated using the formula below.

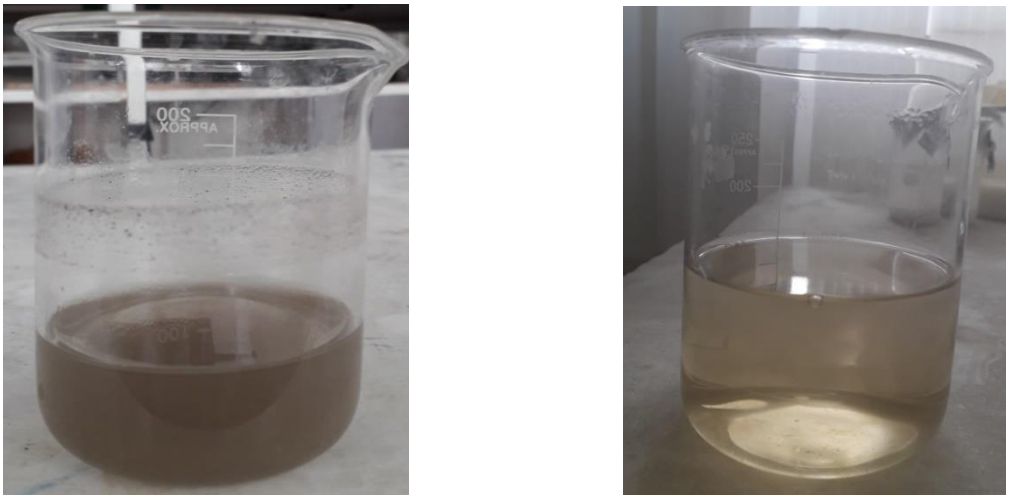
$$molarity = \frac{mass}{molar\ mass} \times \frac{1}{volume} \quad \text{..... Equation 3.3}$$

The calculated mass was dissolved inside 1 liter of distilled water of conical flask and stirred using stirring rod until the pellets were totally dissolved.

The amorphous silica was extracted by leaching with an extraction solution of NaOH at different concentration (0.5, 1.5 and 2.5 M). Ten grams of teff straw ash was added in beaker and NaOH solution was added to it. The beaker was placed in a hot plate with a model of MH2lt. The extraction temperature was varied as (75, 85 and 95°C) and the extraction time was varied as (60, 90, 120 minutes). The mixture was continuously stirred with agitator model of Euro-ST40D5000 at 500 RPM. After extraction the mixture was allowed to cool to room temperature naturally. Then the mixture was filtered using filter paper followed by washing of the residue cake with hot distilled water for maximum bio silica recovery. The liquid part was collected in a beaker and the residue was disposed off.

The reaction was

$4NaOH + nSiO_2(ash) \rightarrow H_2O + 2Na_2O.nSiO_2$



(A) (B)

Figure 3. 6 (A) unfiltered sodium silicate solution (B) filtrated sodium silicate solution

3.2.6 Bio Silica Gel Preparation

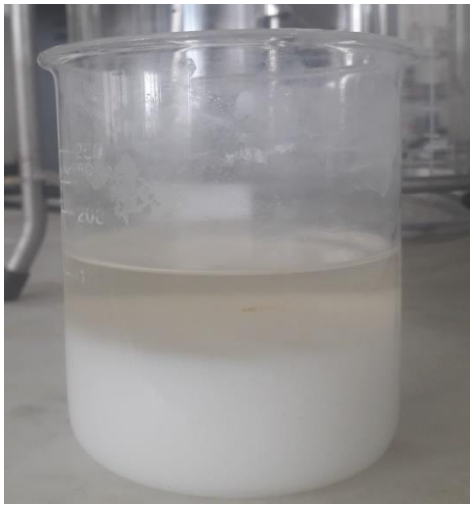
The sodium silicate solution was titrated by adding 2.5 N HCl solution drop wise with an intensive stirring until the pH becomes 10. When the pH reaches 10 the bio silica starts to precipitate. Then the precipitated bio silica solution was heated on a hot plate for 1 hour at a temperature of 80°C and stirred intensively with agitator with 500 rpm. The precipitated bio silica solution was allowed to cool to room temperature and the gel was aged for 20 hours left to intact to promote gel formation. Then the gel was filtered and washed 5 times to remove the soluble salts. Finally the bio silica gel obtained was oven dried at 60°Cover night and the sample was stored in polyethylene bag and later used for characterization. The reaction was

$2\ HCl + 2\ Na_2O.nSiO_2 \rightarrow 2\ NaCl + H_2O + n\ SiO_2\ (S)$

In this stage the silica particles were diffused highly and collision of monomers of silica activated the agglomeration of large silica precipitators.



(A)



(B)



(C)



(D)



(E)

Figure3. 7 (A) Gelification (B) cooling (C) aging (D) filtered silica gel (E) dried silica

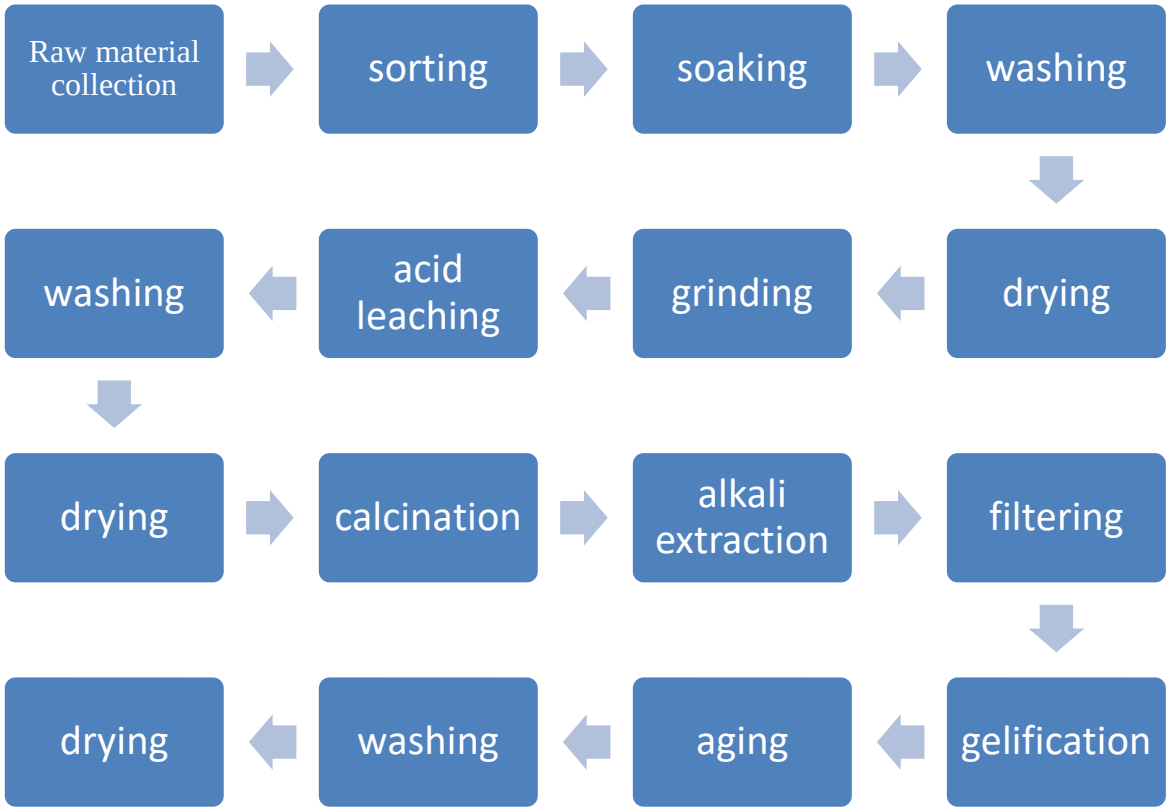


Figure3. 8 Experimental flow sheet diagrams of bio silica preparation

3.2.7 Chemical characterization of TSA and TSAS

A. Chemical content of the teff straw ash (TSA)

In this analysis atomic absorption spectrophotometer (AAS) was used to characterize the chemical constituents of TSA, including major and minor oxides. These analyses were conducted in geochemical laboratory, Ethiopian geological survey.

The potential application of atomic absorption principle is to determine the metallic constituent of silicate materials. The sample being determined through this technique is reduced to elemental state and vaporized. This was done by converting solution of the sample in to fine mist and then drawing it to a suitable flame. Heat of the flame excites outer most electrons to higher orbital which after short intervals of time, return to ground state and a quantum of radiation is emitted. Each element in vapor phase absorbs at a limited number of wavelengths and therefore its absorption spectrum consists of a series of well–defined narrow lines due to the said electronic transactions (Olawale 2012).

B. Fourier Transform Spectroscopy (FTIR)

The functional group of the sample was recorded by FTIR spectra technique. This technique recorded the qualitative characterization of the surface functional group. This analysis was conducted in Leather Industrial Development Institute (LIDI), Addis Ababa, Ethiopia.

C. X-Ray diffraction (XRD)

XRD analysis used to study the phase nature of silica extracted from teff straw ash. The phase nature of the silica is either amorphous or crystalline. Therefore by testing the sample it can be concluded the extracted silica is either amorphous or crystalline. This was conducted in Addis Ababa University, Department of chemistry.

The main use of powder diffraction is to categorize components in a sample by a search/match procedure. Additionally, the areas under the peak are related to the amount of each phase present in the sample.

3.2.8 Silica Yield Calculation

Biosilica yield calculation was performed in order to know the optimum values of experimental variables such as (NaOH concentration, extraction time and extraction temperature) and also to study the effect of each variable. Ten gram of ash was used for the preparation of bio silica. Therefore, the biosilica yield

The SiO_2 yield extracted from teff straw ash was calculated the equation below:-

$$\eta(\%) = \frac{m_{ext} \times 100}{m_{SiO_2}} \quad \text{..... Equation 3.4}$$

Where:-

$\eta(\%)$- is the yield of silica (SiO_2)

m_{ext} (g)- is the mass of SiO_2 obtained

m_{SiO_2} (g)- is the weight of the TSA used in the extraction

3.2.10 Experimental Design

Data analysis was carried out by DESIGN EXPERT version 11 software (Box-Behnken design) to evaluate the effects of the process variables; temperature (75ºC, 85ºC and 95ºC), Extraction time (60min, 90min and 120min) and NaOH concentration (0.5M, 1.5M and 2.5M). The Box-Behnken experimental design prepared 17 experiments on the pattern generated through software. The response variable was bio silica yield. This design of the experiment helps us to

optimize the process parameters for more than three levels and minimize an experimental error that is increased experimental accuracy. Significance of the result was set from analysis of variance (ANOVA). Table below shows the preparation of experiment using design experts version 11 with three level and three factors.

Table 3. 1 Experimental levels and factors with design expert version 11

Run no	Factor 1 A: NaOH concentration(M)	Factor 2 Extraction time (minutes)	Factor 3 Extraction temperature(ºC)
1	0.50	60	85
2	2.50	60	85
3	0.50	120	85
4	2.50	120	85
5	0.50	90	75
6	2.50	90	75
7	0.50	90	95
8	2.50	90	95
9	1.50	60	75
10	1.50	120	75
11	1.50	60	95
12	1.50	120	95
13	1.50	90	85
14	1.50	90	85
15	1.50	90	85
16	1.50	90	85
17	1.50	90	85

3.2.11 Methyl Orange Adsorption Experiment

For the experiment of methyl Orange adsorption the first step was preparation of standard curve. Three different concentration of methyl orange which are (1*10^-5M, 2*10^-5M and 3*10^-5M) solution was prepared and the absorbance of methyl orange was determined using UV-visible spectroscopy with a model of spectro UVD-3000/UVD-3200. Then a standard curve is plotted with concentration versus adsorption. The molarity of the methyl orange solution was calculated by equation 3.3.

Methyl orange adsorptions were conducted in magnetic stirrer under room temperature and 25 ml volume of methyl solution was added in 50 ml beaker with initial concentration of 3*10^-5M. The adsorbent dosage was 0.1 gram. It was stirred in magnetic stirrer for 4 hours under 250 rpm. The solution was centrifuged in a centrifugation machine for 10 minutes. The absorbance capacity of the centrifuged solution was measured using UV-visible spectroscopy at wavelength of 460nm. And the residual concentration of methyl orange was calculated from the standard curve. The percentage removal of methyl orange was calculated using equation 3.5 (D.R.TCHUIFON 2014).

$$\%R = \frac{C_o - C_t}{C_o} \times 100 \quad \text{..... Equation 3.5}$$

Where %R - the percentage removal

C_o - is the initial concentration of methyl orange

C_t - is the concentration of methyl orange after adsorption

CHAPTER FOUR

4. Result and Discussion

For this section a result and discussion for production and evaluation of silica from teff straw and the effect of each variable is analyzed.

4.1 Raw Material Characterization

4.1.1 Moisture Content of the Raw Teff Straw

The moisture of the teff straw was measured as it was received immediately and it was calculated by using equation 3.1. The experiment was repeated three times and the result is displayed in the table below. The initial mass of the teff straw was 5 gram and dried in an oven until constant mass was obtained. From the table below the average moisture content of the raw teff straw was 8.13 ± 0.7. From this the moisture content of the teff straw was similar to the literatures discussed (Ayana Bekana Bageru 2018) and the teff straw contains small amount of moisture which contributes a high advantage on the ashing process.

Table 4. 1 Moisture content of raw teff straw

Run no.	Teff straw mass after drying	Moisture content %
1	4.63	8
2	4.65	7.5
3	4.59	8.9

4.1.2 Determination of Ash Content

The content of biomass varies depending on soil chemistry, nature of biomass and climate condition including geographical location. Since silica is obtained from the ash of the teff straw it is important to calculate how much amount of ash is obtained after the thermal decomposition of the treated teff straw. The experiment is repeated three times and the result is displayed in the table below. The amount of ash obtained was calculated using equation 3.2.

The ash content of the teff straw is 4.073 ± 0.24 which favors bio silica production.

Table 4. 2 Ash content of teff straw

Run number	Teff straw ash %
1	4.3
2	3.82
3	4.1

4.2 Reaction Mechanism

After the preparation of teff straw ash, the process goes on with some reactions. Since the precursor for sol-gel process is sodium silicate or sometimes called water glass the step after the thermal decomposition was synthesis of sodium silicate solution. The process goes on with the reaction of recovery, hydrolysis and condensation reaction.

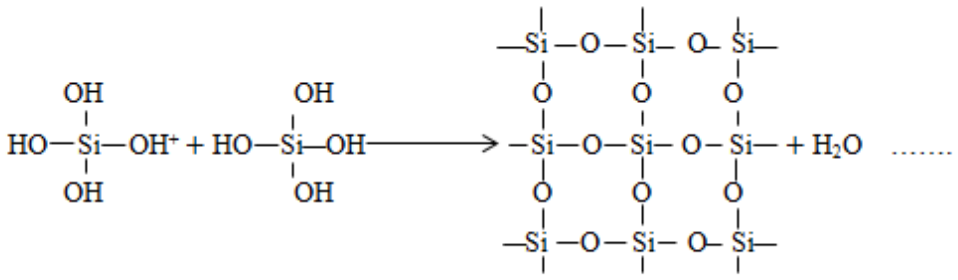
When the teff straw ash reacted with sodium hydroxide the reaction process called recovery stage. In this reaction the silica in the ash is reacted with sodium hydroxide and results in the production of sodium silicate and water.

$SiO_2 + 2\ NaOH \longrightarrow Na_2SiO_3 + H_2O$ ……equation 4.1

The second step was titration of sodium silicate with hydrochloric acid to form silanol group and sodium chloride. This reaction is called hydrolysis reaction.

$$Na_2SiO_3 + H_2O + 2\ HCl \longrightarrow HO-\underset{\displaystyle OH}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{Si}}}}-OH + 2NaCl$$ …… equation 4.2

When the silica precipitated the last stage after washing was condensation reaction.



…… equation 4.3

4.3 Characterization of the TSA and Extracted Silica

4.3.1 Chemical Content Analysis of the Teff Straw Ash

Table 4.3 shows the major and minor oxides of the TSA (teff straw ash) sample. Based on the result reviled by AAS (atomic absorption spectrophotometer) the major constituent of the ash sample was SiO_2. Small amount of Fe_2O_3, CaO, K_2O, P_2O_5, H_2O were also present along with traces of Al_2O_3, Na_2O, TiO_2, and MgO. LOI is loss on ignition during the process of analyzing the percentage composition of the silica.

Table 4. 3 Chemical composition of TSA

Constituents	Constituents (%)
SiO_2	92.18
Al_2O_3	<0.01
Fe_2O_3	0.26
CaO	1.78
MgO	0.54
Na_2O	<0.01
K_2O	0.1
MnO	<0.01
P_2O_5	0.34
TiO_2	<0.01
H_2O	1.5
LOI	2.33

It is evident that chemically the teff straw ash composed of silicon compounds in large amount. Bageru and Srivastava reported that the amount of silica from brown teff straw at ashing temperature of 700^0C and ashing time of 2 hours was 91.2%. In the present study the amount of silica in the ash is a little bit higher which 92.18%. This is due to the soil chemistry, nature of biomass and climate condition varies the content of the biomass. (wassie and Srivastava). Since the cultivation area of the teff straw used in the research is different from the above literature (Bageru and Srivastava) the cause of the increment of the percentage of the silica in the present

study is due to the soil chemistry of the cultivated area and the composition of the amount of the brown teff straw which is a mixture of white and black teff straw. Teff grain comes in a range from milky white to almost dark brown. The most common colors are white, creamy white, light brown, and dark brown (Bultosa 2007). Since there are varieties of teff in Ethiopia consequently the amount composition of the teff straw will vary. This resulted in the composition difference of the teff straw ash.

4.3.2 Fourier Transform Spectroscopy (FTIR)

The major chemical groups present in silica are identified by the FTIR spectra shown in Figure (4.1). The FTIR spectra were performed in the range from 4500 to 400cm^{-1}.The region 1950-1766 cm^{-1} is attributes to an over tone structure vibration. Because it remains unaffected by different treatments, its integrated value is used as a reference band to normalize all other intensities. The vibrations in the range of 3100-3800 cm^{-1} is due to the O-H bond present in the silanol group (Si-OH). It is caused by the adsorbed water molecules on the silica surface. When we see in detail the small region between 3400-3100 cm^{-1} is the trapped water in the silica. The region in the range of 3100-3800 cm^{-1} is small because the silica product is dried in an oven for long time and the H_2O is evaporated. So the bio silica contains small O-H group. In the region 1850-3100 cm^{-1} there is no strong peaks except very small peak at 2372 cm^{-1}. This shows that the absence of Si-C stretching bond. This confirms that there is no significant organic compound in the product due to the controlled combustion and extraction processes. The FTIR result shows a strong band in the range of 1050-1230 cm^{-1}. This is caused by the presence of Si-O-Si asymmetric band stretching. The peak at 795-800 cm^{-1} is due to the presence of Si-O bending vibration and the peak at 445–488 $cm^{-1}$is due to Si–O out of plane bending vibrations (Ayana Bekana Bageru 2018). The FTIR analysis achieved here in this experiment is similar to those reported by other workers who carried out similar studies.

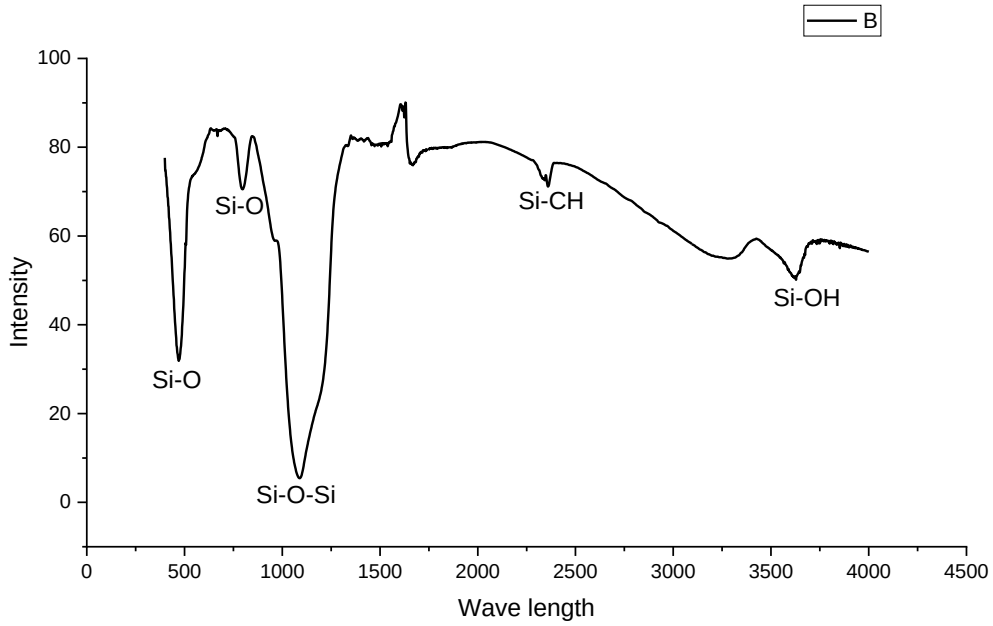


Figure 4. 1 FTIR spectra of synthesized silica from teff straw

4.3.3 X-Ray Diffraction (XRD)

The peak height of XRD result shows that concentration of dominating phases with higher concentration by higher peaks. The major reflections or peaks of crystalline quartz from ICSD powder diffraction files (PDF) occur at Bragg 2θangles of 20.856˚, 26.636˚and 36.541˚ (Addis Lemessa Jembere 2017). It can be seen that no defined peaks corresponding to these Bragg 2θangles are found in Figure 4.2. A rather broad peak spanning 2θ angle range of 18-30ºwhich is characteristic of amorphous structures is observed. The XRD diffractogram shows that the silica was primary in amorphous form as indicated by a broad peak height centered on 2θ angle. The amorphous structure of biosilica is indicated by at peak position of approximately 23° on the diffractogram. The presence of crystal silica can only be identified if the XRD result contains sharp peaks along with broad peak. In the present case no sharp peak is present which indicates very low percentage of crystal silica. The acid treatment performed on natural teff straw has no effect on the crystalline domains. The calcination temperature and time are significant factors that express the amorphous and/or crystalline silica content in teff straw ash silica (TSAS). Long time and a high calcination temperature cause the crystallization of the amorphous silica. This is due to the presence of potassium and sodium in the ash which accelerates melting of the particles and leads to crystallization of the silica. However this phenomenon was not observed in this

study because the maximum temperature applied was 700^0C. According to (Ayana Bekana Bageru 2018) the crystallization of the silica occurs at temperature more than 700^0C.

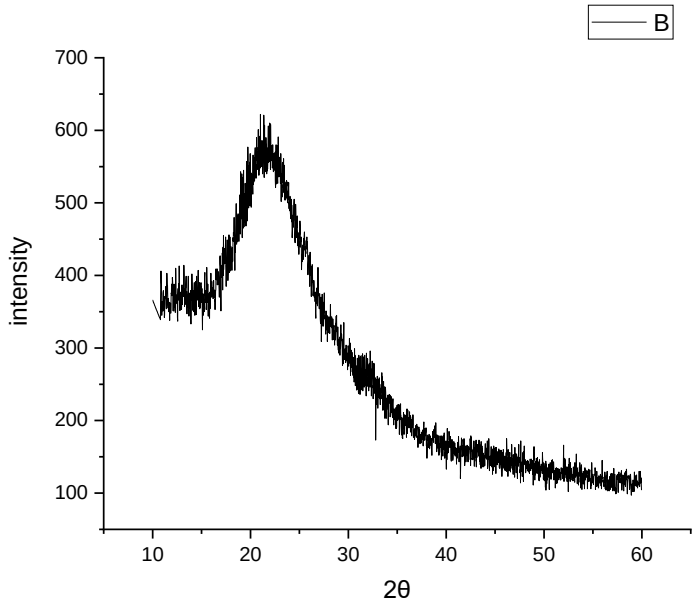


Figure 4. 2 XRD pattern of silica sample from teff straw

4.4 Silica Yield Result and Effect of Process Parameters on the Extraction of Silica

4.4.1 Silica Yield

The yield of the silica was calculated using equation of 3.4

As it is discussed in the methodology to find the optimum operating process variables of pure silica as maximum, the yield mass must be weighed after the final drying process for each run. The yield of the mass percentage was given in the table below. The maximum yield was 83% and the minimum was 48.8%.

Table 4. 4 Experimental silica yield from teff straw

Run	NaOH concentration (M)	Extraction time (minutes)	Extraction temperature (^{0}C)	Yield (%)
1	0.5	60	85	48.8
2	2.5	60	85	72
3	0.5	120	85	53.5
4	2.5	120	85	75
5	0.5	90	75	50

6	2.5	90	75	72.9
7	0.5	90	95	52
8	2.5	90	95	75
9	1.5	60	75	78.6
10	1.5	120	75	81.8
11	1.5	60	95	80
12	1.5	120	95	83
13	1.5	90	85	80.3
14	1.5	90	85	80.9
15	1.5	90	85	80.2
16	1.5	90	85	79
17	1.5	90	85	80.3

4.4.2 Statistical Analysis for the yield of silica

This design of the experiment helps us to optimize the process parameters for more than two levels and minimize an experimental error that is increased experimental accuracy. Initially Box-Behenken experimental designs were used to obtain the model equation. As usual, the experiments were performed in random order to avoid systematic error. Significance of the result was set from analysis of variance (ANOVA). The symbol terms in ANOVA were listed below:-

A = NaOH concentration

B = extraction time

C = Extraction temperature

AB = the interaction between NaOH concentration and extraction time

AC = the interaction between NaOH concentration and Extraction temperature

BC = the interaction between extraction time and Extraction temperature

Table 4. 5 ANOVA of fitted model for the yield of bio silica

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2438.43	9	270.94	709.12	< 0.0001	Significant
A-NaOH concentration	1026.05	1	1026.05	2685.48	< 0.0001	

B-Extraction time	24.15	1	24.15	63.21	< 0.0001
C-Extraction temperature	5.61	1	5.61	14.69	0.0064
AB	0.7225	1	0.7225	1.89	0.2115
AC	0.0025	1	0.0025	0.0065	0.9378
BC	0.0100	1	0.0100	0.0262	0.8760
A^2	1378.65	1	1378.65	3608.35	< 0.0001
B^2	0.3301	1	0.3301	0.8640	0.3836
C^2	0.7785	1	0.7785	2.04	0.1965
Residual	2.67	7	0.3821		
Lack of Fit	0.7425	3	0.2475	0.5124	0.6952 not significant
Pure Error	1.93	4	0.4830		
Cor Total	2441.10	16			

Table 4.5 showed that the effect of NaOH concentration, extraction time and extraction temperature and also the interaction effect between NaOH concentration and extraction time, NaOH concentration and Extraction temperature and extraction time and extraction temperature. The P values were used as a tool to check the significance of each of the coefficients, which in turn are necessary to understand the pattern of the mutual interactions between the test variables. The larger the magnitude of F-test value and the smaller the magnitude of P-values, the higher the significance of corresponding coefficient. Values of P less than 0.05 indicate that the model terms are significant. In this case the three factors which are the NaOH concentration, extraction time and extraction temperature are significant model terms and have a high effect on the yield of the product. Values greater than 0.0500 indicate the model terms are not significant. Therefore the interaction effects between all three factors are not significant. To improve the model the insignificant model terms were reduced. The table below is a modified statistical analysis when the insignificant model terms are eliminated.

Table 4. 6 Modified ANOVA of fitted model for the yield of bio silica

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2436.53	4	609.13	1597.82	< 0.0001	Significant
A-NaOH concentration	1026.05	1	1026.05	2691.43	< 0.0001	
B-Extraction time	24.15	1	24.15	63.35	< 0.0001	
C-Extraction temperature	5.61	1	5.61	14.72	0.0024	
A^2	1380.72	1	1380.72	3621.78	< 0.0001	
Residual	4.57	12	0.3812			
Lack of Fit	2.64	8	0.3303	0.6839	0.7005	not significant
Pure Error	1.93	4	0.4830			
Cor Total	2441.10	16				

Fit Statistics

Std. Dev.	0.6174	**R^2**	0.9981
Mean	71.96	**Adjusted R^2**	0.9975
C.V. %	0.8580	**Predicted R^2**	0.9965
		Adeq Precision	100.6209

The "Model F-value" of 1597.82 implies the model is significant relative to the noise. There is only 0.01% chance that a "Model F-value" this large could occur due to noise.

The fitness of the model equation was also expressed by the coefficient of determination, R^2. The adequacy of the model was tested by analysis of variance. The value of R-squared for the developed correlation was 0.9981. It implies that 98.19% of the total variation in the percentage of silica yield is attributed to the experimental variables studied. This model is used to navigate the design space.

The final equation in terms of codded factors:

$$\textbf{silica yield} = +80.46 + 11.33 \times A + 1.74 \times B + 0.84 \times C - 18.06 \times A^2$$

4.4.3 Model Adequacy Check

A line of unit slope, i.e. line of perfect fit with points corresponding to zero error between predicted values and actual values are also shown in Figure 4.3. This plot therefore, shows the performance of the correlation in an obvious way. The results in Figure 4.3 demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all points are very close to the line of perfect fit. This result indicates that it was successful in capturing the correlation between the three silica production process variables to the silica yield.

The adequacy of the model was further checked with the analysis of variance (ANOVA) as shown in the Table 4.6. Based on a 95% confidence level, F-value is a test for comparing model variance with residual (error) variance. If the variances are close to the same, the ratio will be close to one and it is likely that any of the factors have a significant effect on the response with the P-value greater than 0.05. It was calculated by model mean square divided by residual mean square. Here the "Model F-value" of 1597.82 implies the model is significant relative to the noise. There is only 0.01% chance that a "Model F-value" this large could occur due to noise.

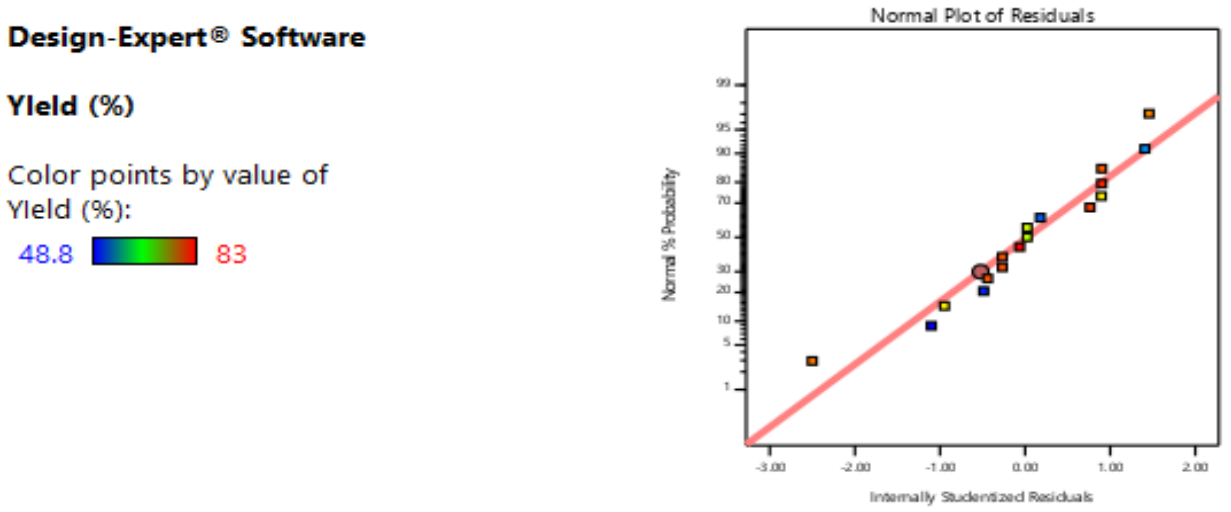


Figure 4. 3 Predicted versus the actual yield of silica

A line of perfect fit with points corresponding to zero pure error between predicted values and actual values of the silica yield were. This plot therefore, shows the performance of the correlation in an obvious way. The above figure demonstrated that the regression model equation provided the actual and predicted values were the same description of the experimental data, in which all points are the same close to the line of perfect fit.

4.4.3 The Effect of NaOH Concentration on the Extraction of Silica

It was noted from the preliminary experiments the amount of silica gel was highly dependent on the concentration of sodium hydroxide solution. In this study, to explore the optimum conditions for maximum of silica from teff straw, the concentration of sodium hydroxide solution was varied systematically. As shown in the figure below the concentration was varied from 0.5M to 2.5 M.

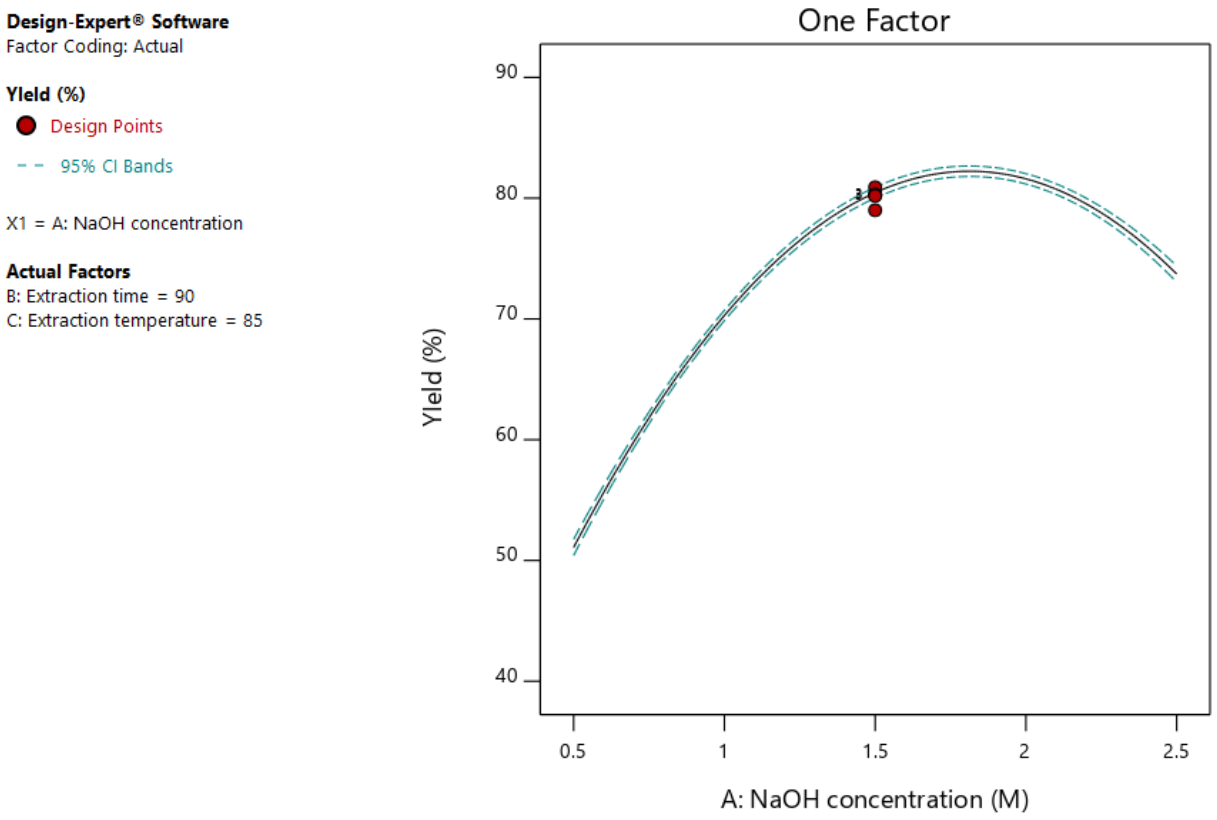


Figure 4. 4 Effect of NaOH concentrations on the extraction of silica

Results in the above figure showed that the amount of the extracted silica was small at 0.5M concentration of sodium hydroxide. This means that the silica in the TSA was not fully dissolves in the solution. In other words there was limitation of Na to prepare sodium silicate solution ($2Na_2.nSiO_2$) However, the extracted amount of silica shows significant increase when the concentration of sodium hydroxide was increased to1.5M. But when the concentration of sodium hydroxide becomes 2.5M, the extracted amount of silica significantly decreases. This is happened because after the maximum yield, the increase in concentration of NaOH solution to 2.5 M leads to the formation of viscous sodium silicate solution. Then excess NaCl and OH^- is formed in the solution during titration. The increase of NaCl molar concentration over that of

silicate induces an increase in solution viscosity by neutralizing the charge of silicate oglinomers and micelles. This increase in solution viscosity apparently reduces the diffusion of molecules and prevents silicate oglinomer collision, which consequently did not allow for polymerization during the gelification process.

This difference in the amount of the extracted silica suggested the fact that the regional variation had obvious effect on the silica content of the TSA and should be taken into consideration before using TSA for the extraction of silica on the commercial bases.

The selection of the minimal level depends on the pH of the sodium hydroxide solution. As it is described in the early studies the authors specified that silica is only soluble in sodium hydroxide solution greater than pH of 10. Even though the pH of 0.5 M of sodium hydroxide is 13.69 at room temperature, the pH of the solution decreases at higher temperatures. Therefore the pH of o.5 M of NaOH solution decreases up to almost 10, because in this study the minimum temperature used were 75^{o}C. The maximum level selection is based on viscosity of the sodium silicate solution. When the concentration of NaOH solution is greater than 2.5M, the sodium silicate solution becomes more viscous. More viscous sodium silicate solution leads to less yield of silica. Therefore 2.5 M of sodium hydroxide is selected.

4.4.4 The Effect Extraction Time on the Extraction of Silica

The extraction time is one of the important factors that can affect the yield of silica. In this study the extraction time varies from 60 minutes -120 minutes. The selection of the minimum and maximum levels depends on earlier studies of extraction of silica from biomass. Time which is below 60 minutes of extraction time yields with a negligible mass of silica. (Ikram Ul Haq 2014)Which means extraction time less than 60 min is not enough for solubility of silica in the TSA. And increasing extraction time above 120 minutes is not economical.

The figure below indicates that the silica yield at 60min, 90 min and at 120 min was 78.7%, 80.2% and 82.2% respectively. The maximum yield of silica was happened at 120 min extraction time. Thus under the applied experimental conditions increasing the extraction time increases the yield of silica. That means 120 minutes is not the extraction time to reach its limiting value or means more time is needed to dissociate all the silica available in the ash.

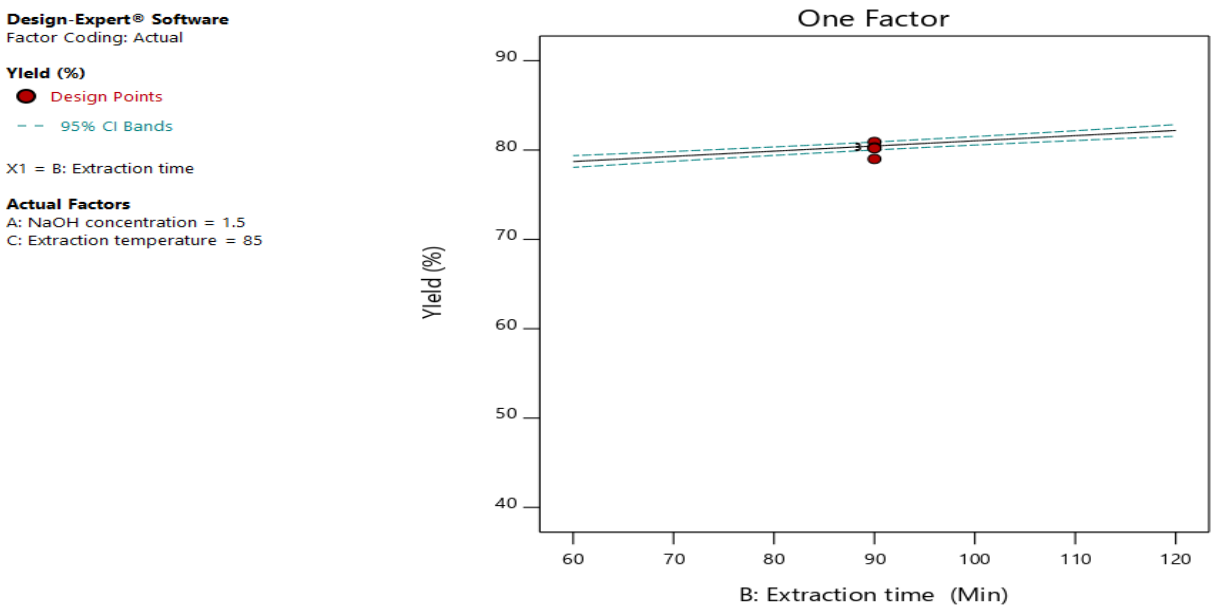


Figure 4. 5 Effect Extraction Time on the Extraction of Silica

4.4.5 The Effect Extraction Temperature on the Extraction of Silica

Temperature is one of the factors which affect the yield of silica. As shown in the figure 4.6 the yield of silica varies in small range. The output yield was 79.6%, 80.2% and 81.29 % respectively for the extraction temperature of 75^0C, 85^0C and 95^0C. The yield of silica increases with increasing temperature in small amount. Higher temperature decrases the viscosity of sodium silicate and increases the rate of reaction.

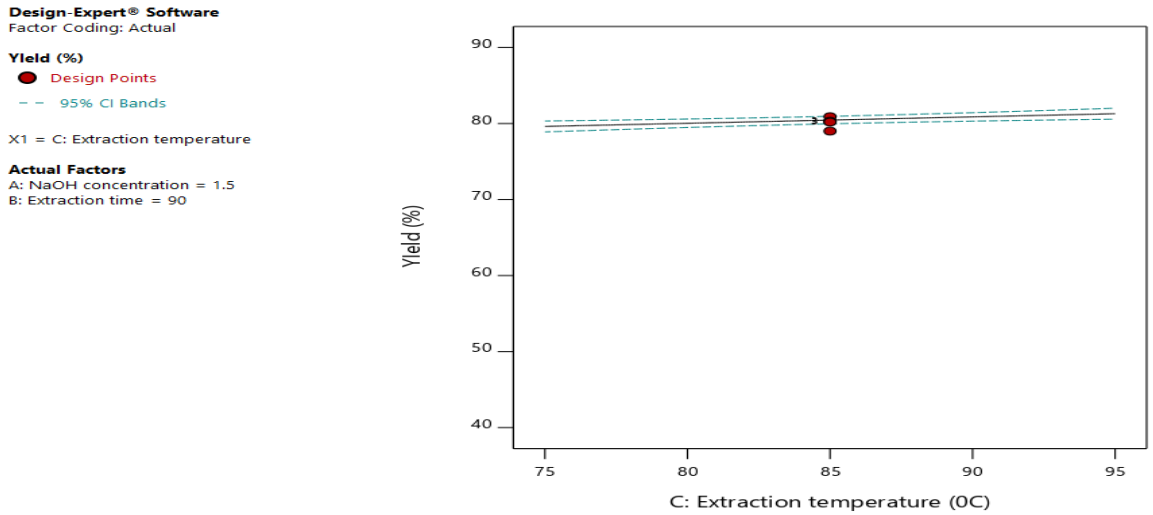
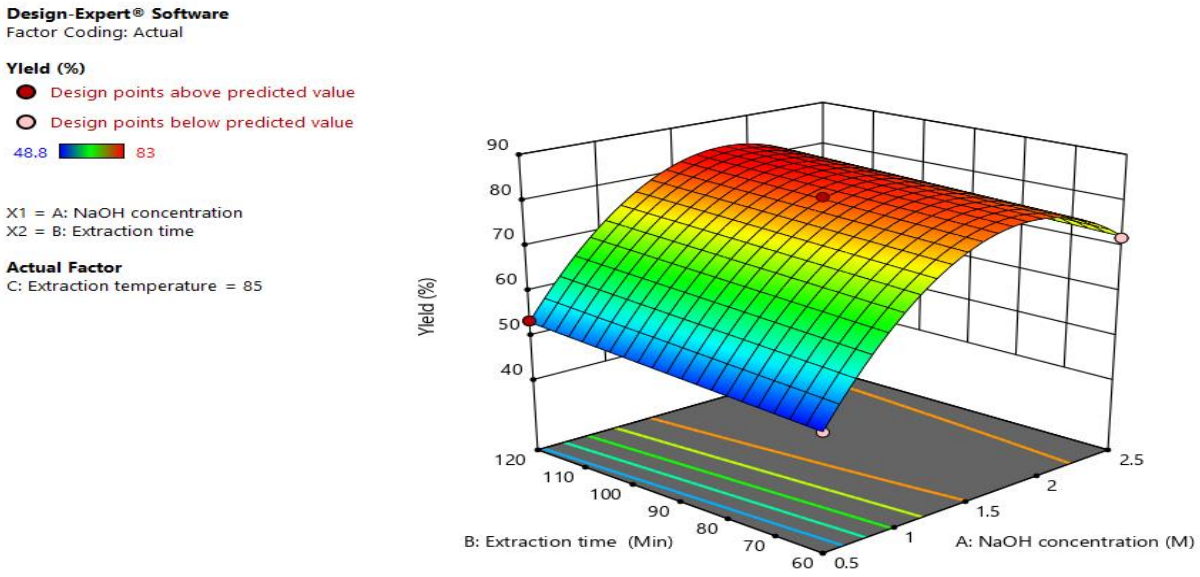


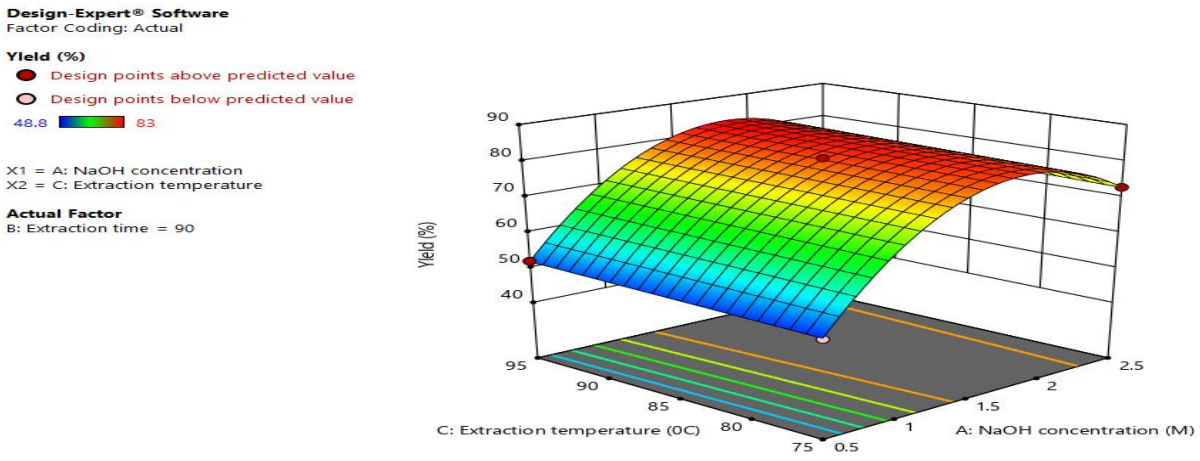
Figure 4. 6 Effect of temperature on the extraction of silica

4.4.6 Interaction Effect on the Yield of Silica

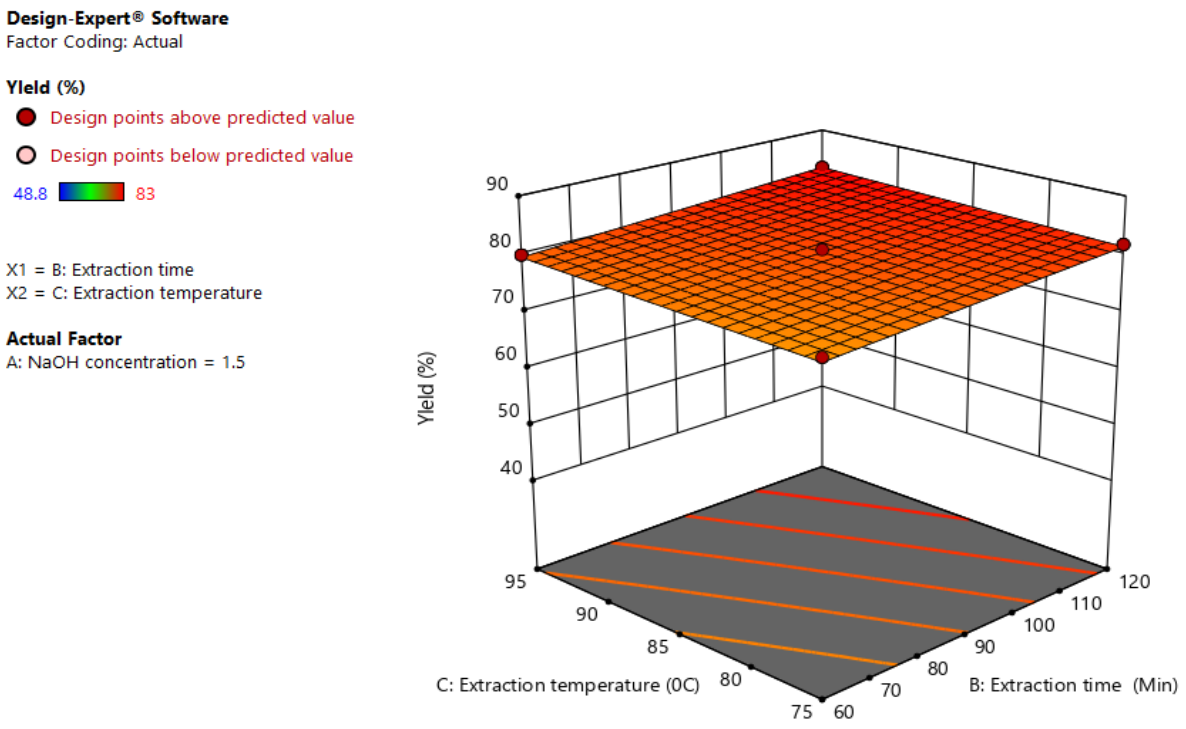
The study of the effects of the combinations of three factors were discussed and some important results described in the contour diagrams in figure below (figure 4.7). The result shows that there is no any interaction effect between those factors and act independently on the silica yield.



(A)



(B)



(C)

Figure 4. 7 (A) interaction effect between NaOH concentration and extraction time, (B) interaction effect between NaOH concentration and extraction temperature and (C) interaction effect between extraction time and extraction temperature

4.4.7 Optimal Silica Yield Process Parameters to Prepare Maximum Silica Yield

Preliminary observations show that silica yield varies significantly according to the experiment parameters, reaching values of 48.8-83% under certain operating conditions. To find the optimum extraction process parameters for the highest silica yield, the extraction process parameters were optimized subject to constraint shown in the figure below. Five solutions were found and the solution with the highest yield was chosen. The maximum yield was 83.23% under the optimum process variables of 1.79M of NaOH, 109.99 minutes and 84.17^0C. In other to verify the optimization results, the selected parameters were validated in the laboratory with suggested process parameters. The result from the experiments confirmed the selected solutions.

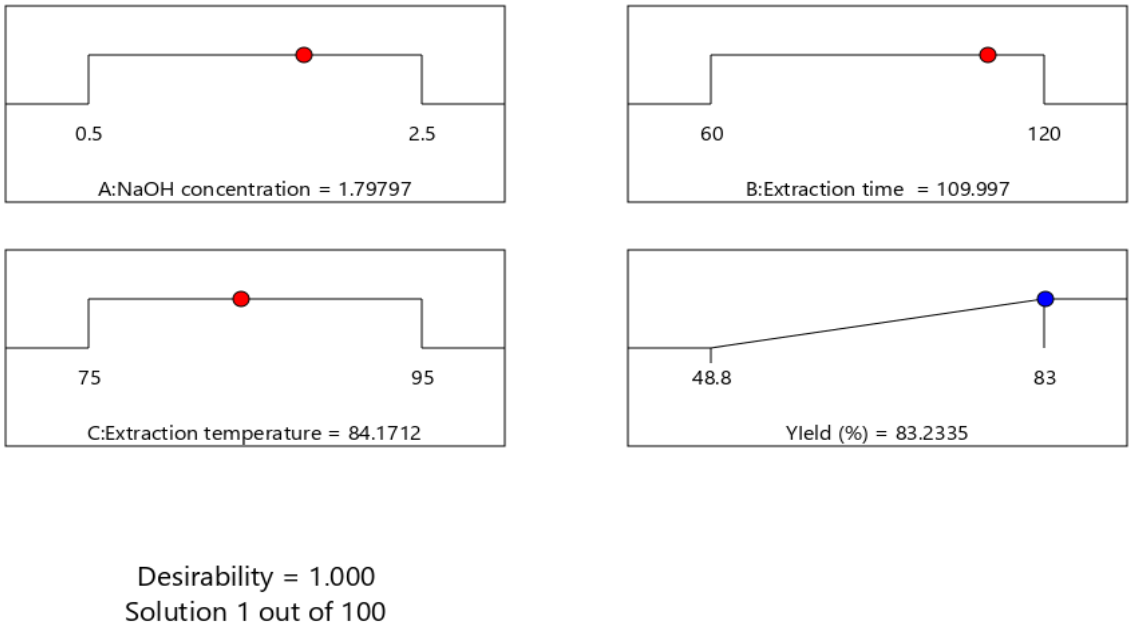


Figure 4. 8 Optimization constraints and solutions for extraction of silica

4.5 Methylene Orange Adsorption

The XRD and AAS analysis show that the prepared samples contain high amount of silica. It is also seen in the FTIR analysis that the samples possess silica functionalities. Considering the fact that the silica functionalities can interact with the polar groups of other pollutants through strong H-bonds and complex mechanisms, the prepared silica sample were tested for the adsorptive removal of methyl orange from aqueous solution.

The first step in the adsorption experiment was preparation of standard graph. The graph consists of methyl orange concentration versus its adsorption. The result is shown in the table below.

Table 4. 7 Adsorption result

Methyl orange concentration	**Adsorption**
$1*10^{\wedge -5}$	0.191
$2*10^{\wedge -5}$	0.221
$3*10^{\wedge -5}$	0.263

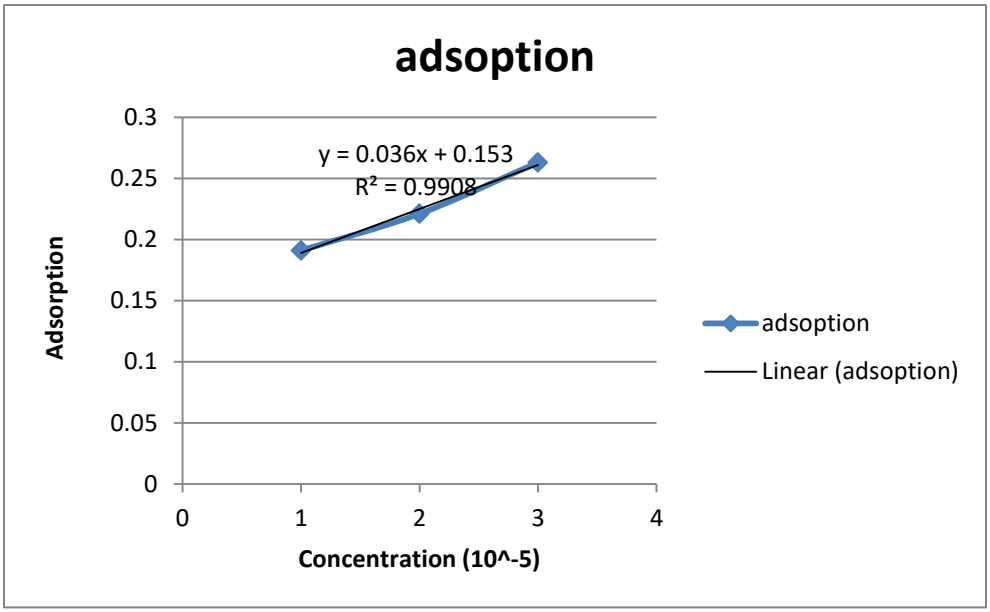


Figure 4. 9 Methyl Orange Concentrations versus Adsorption

From the above figure the R^2 value is 99 %. This implies that 99 % of the total variation in the adsorption is attributed to the experimental variables studied. The model equation is

$$y = 0.036x + 0.153 \quad \text{..... } \textit{Equation 4.2}$$

Where y- adsorption

x- Concentration of methyl orange

After adsorption experiment was performed the treated methyl orange solution was measured its adsorption capacity by using UV- visible-spectroscopy and the concentration of the residual methyl orange in the solution was calculated using the model equation of 4.2. In order to know the removed percentage of methyl orange by the prepared silica equation 3.5 was used.

From table 4.8 the average removal efficiency of methyl orange using prepared silica was 82.77$\pm$2.8%. The teff straw ash silica adsorbs methyl orange because it is porous material and also has an active group that is Si-O-Si and Si-OH.

Table 4. 8 Treated methyl orange adsorption result

Run no.	**Adsorption**	**Concentration MO after treatment**	**% removal**
1	0.175	0.61*10^-5	79.7
2	0.169	0.44*10^-5	85.3
3	0.171	0.5*10^-5	83.3

CHAPTER FIVE

5. Conclusion and Recommendation

5.1 Conclusion

In this study experiments were conducted to investigate the potential of teff straw for the production of bio silica. Present experimental results show that teff straw is potential and renewable source for silica relative to previous studies under similar conditions. Amorphous form of silica was successfully extracted from teff straw ash with high purity and yield. Teff straw sample preparations and bio silica harvesting via sol gel method is simple, green and economical. The physical analysis shows that teff straw ≈4% ash and ≈8%as moisture. AAS analysis shows that teff straw ash contains considerable amount of silica up to 92%at 700°C for 2 hours ashing time. The prepared silica exhibited FTIR spectra peaks which are similar to the literatures discussed XRD pattern showed that the sol-gel process potentially eliminates almost all other constituents, and only amorphous silica was synthesized.

The highest bio silica yield and a model for the yield were investigated by means of Box-Behenken design. The result presented herein provides clear evidence that the NaOH concentration and Extraction time influence greatly the yield of silica, while the extraction temperature has less effect than the other two factors. The investigated parameters do not exert binary interactions and they are neglected on the model equation. The experimental data showed that 1.5M, 95^{o}C and 120 minutes are the best parameters for the maximum yield of bio silica from teff straw. When the concentration of sodium hydroxide becomes 2.5M, the extracted amount of silica significantly decreases. Under the applied experimental conditions increasing the extraction time and extraction temperature increases the yield of silica.

This prepared silica was further tested for the adsorptive removal of methyl orange from aqueous solution and has a removal efficiency of 82.77$\pm$2.8%.

In general this raw material further substantiates that teff straw ash is economically beneficial and promising bio-precursor for preparation of silica via rapid, eco-friendly, and inexpensive sol-gel method and can replace the synthetic silica.

5.2 Recommendation

The main outcome of this research is amorphous silica from aboundantly available teff straw. This produced amorphous silica used for the different applications but in this research paper is used as an adsorptive material. Some of the applications of amorphous silica is as rubber and tire fillers , as an adhesive, as extender in production of detergents and others. If some further research work is carried out to explore the potential of teff straw,
recommended studies are listed below:

- Since effect of other parameters such as burning time, and burning temperature affects the yield and structure of silica a detail study should be conducted.
- Reserches should be done on the sluge reemoval of the residue carbon during filteration and recycling to a useful material
- The effect of bleaching acid type and concentration on the yield of silica should be studied in detail
- It is recommended to perform preliminary design, economic feasibility study and establish economic scale for production of bio silica from teff straw
- It is recommended to study the enrgy recycling durinh the extraction of silica

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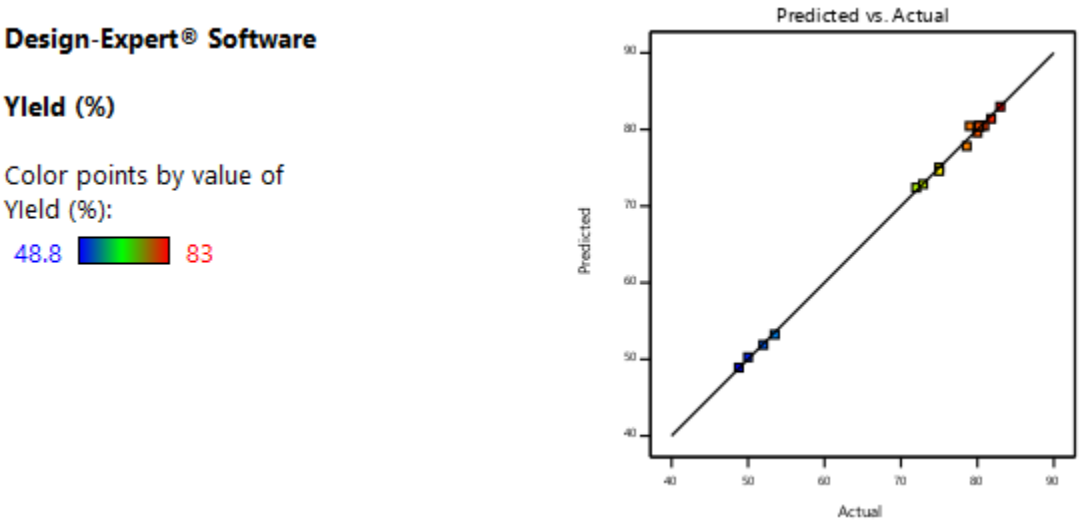
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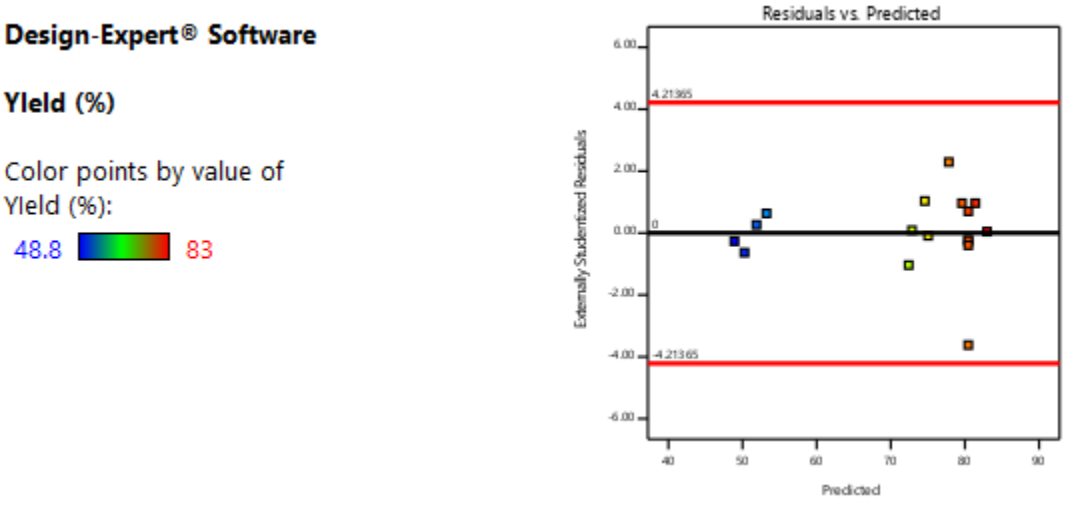
Appendices

A. Fit Summary and diagnostics of responses

Response 1: YIeld (%)

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	0.0544	< 0.0001	0.3016	-0.0549	
2FI	0.9999	< 0.0001	0.0925	-1.3613	
Quadratic	**< 0.0001**	**0.6952**	**0.9975**	**0.9939**	**Suggested**
Cubic	0.6952		0.9968		Aliased





B. Pictures of some laboratory works



Grinded teff straw



Cooling of leached teff straw



Removal of calcined teff straw ash from furnace



Filtration of SSS