ADDIS ABABA UNIVERSITY

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School of Chemical and Bio Engineering

Environmental Engineering Stream MSc. Program

synthesis of silica xerogel from bottom ash of Reppi waste to energy as a Methylene blue adsorbent on Textile wastewater

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By

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A thesis submitted to School of Chemical and Bio-engineering, Addis Ababa institute of Technology, Addis Ababa University for partial fulfillment of Master of Science in chemical (environmental) Engineering.

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A Thesis submitted to the school of Chemical and Bio Engineering in partial fulfillment of the requirements of the Degree of Masters of Science in Chemical and Bio Engineering (Under environmental engineering stream).

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List of acroniums

BA	Bottom ash
BOD	Biylogical oxygen demand
COD	Chemical oxygen demand
EBA	Extracted bottom ash
TBA	Treated bottom ash
BET	Brunauer-Emmett-Teller
LOI	Loss on iginition
LOD	Loss on dissolution
MB	Methylene blue
MSWBA	Municipal solid waste bottom ash
TSS	Total suspended solid
TS	Total solid
FTIR	Fourier transform infrared

Abstract

Dyes are water soluble complex organic compounds, it present in the textile dyeing process and they are nonbiodegradable waste in the textile wastewater. In Ethiopia, most textile factories are located nearby water bodies and they discharge their color effluent to canals, rivers, lakes, and streams without treatment. Those Effluents can harm all forms of living things. Among those dyes discharging MB dye without treatment can affect human life and aquatic life. The aims of this research were to synthesis silica xerogel from bottom ash by the sol-gel process to treat dyehouse waste. In this study the first stage was the leaching treatment to reduce heavy metal elements and to increase silica extraction, the second step was extraction process was employed to synthesize sodium silicate at different parameters such as extraction time (1, 2, and 3h), NaOH concentration (1, 2 and3M) and solid to liquid (wt: vol) ratio (1:1, 1:2 and1:3) with constant temperature 75^0c. Since the sol-gel process for all extracted sodium silicate were done at the same parameter such at room temperature, hydrosol pH 3, the addition of water 40mL slow constant stirring, 18h aging time, drying at 105^0c for 24 hr and final silica gel pH7. The High percent of purity (84.1321%) of silica gel was obtained with the ratio 1:1.5, 2:5hr, and 2M of NaOH concentration with 0.901 desirability chosen as optimal sodium silicate extraction parameter.

The physical and chemical characteristics of the mesoporous silica materials were analyzed using BET, FTIR and also their purity, moisture content, and bulk density was characterized. The results indicated that the BET surface area and pore diameter of the synthesized silica materials were 253.1 m^2/g and 18.38Å; respectively. The FTIR spectra confirmed the existence of a surface hydroxyl group and the occurrence of symmetric Si–O stretching. The results indicate that purity, moisture content, and bulk density were 84.13, 5.26%, and 0.73gm/cm^3 respectively. Under the experimental conditions at 30.85 min, 0.1g silica gel dosage for 13.94mg/L dye concentrations were found for maximum dye removal efficiency (86.101%) with0.99desirability. The optimal condition was checked on textile dye house water, which dye concentration was 14.81mg/L, the result becomes 84.62% dye removal efficiency. Consequently, the experimental results indicated that the bottom ash has the potential to be used as silica gel for dye removal.

Keywords: silica gel, Methylen blue, bottom ash, and removal efficeincy

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Chapter One

Introduction

1.1 Background

The development of fashion trends has pushed the textile industry to grow rapidly. Textile industry is a very diverse sector in terms of raw materials, processes, products and equipment and has very complicated industrial chain. These industries have an impact on the environment especially on water pollution, textile wastewater contains non-biodegradable organic and inorganic materials such as dyes, metals ,phosphates,aerosols,high COD and BOD concentration, surfactants and phenols. Due to usage of dyes and chemicals, effluents are dark in color, which increase the turbidity of the water body. The main pollutants in textile industries came from dyeing and finishing section. Dyes are widely used as one of the key ingredients in many industries like textile, paint and varnish etc. These industries discharged the dye in the environment with their wastewater, and one of the major problems concerning textile wastewater is the highly colored effluent, which can be difficult to decolorize. The main environmental concern with dyes is their absorption and reflection of sunlight entering the water and thus causing reduction in photosynthesis (D. Ingrachen-Brahmi et al., 2020).

Around 15% of the total dye production in the world is used by the textile industry and its waste is discharged into the environment (Houas et al., 2001). Textile dyes in the form of organic compounds that are nonbiodegradable. One of the common dyes is methylene blue ($C_{16}H_{18}N_3SCI$) because; this dye has several advantages such as the price is relatively cheap, easy to obtain, good solubility, and is a basic dye. In the coloring process, methylene blue is bonded about 5% while the remaining 95% is wasted as waste, so the presence of dye in water systems limits the diffusion of sunlight through the water bodies and thus prevents photosynthesis in aquatic plants, impedes the growth of bacterial and causes a harmful effect to humans such as skin irritation, mutation, allergic, dermatitis, cancer, etc (Gong J.et.al., 2015). Among various treatment methods available for dye removal, the adsorption has been proved to be the most suitable and promising technologies or has become the most popular technique because of its effectiveness, operational simplicity, low cost and low energy requirement

(F.N.Allouche et al.,2015) It is also a highly efficient technology and easily adaptable with many ubiquitous materials being used as an adsorbent in the process. Among the several adsorbents which have been used as adsorbent during the adsorption process such as activated carbon, silica gel, fly ash and clay etc. The effort has continued to explore the suitability of materials as adsorbent because of the presence of large pore and surface area (A.S. Kovo, *et al,2018).*

Xerogel adsorbent is a solid formed from a gel, which are being prepared through drying slowly at room temperature with an unconstrained shrinkage (Czarnobaj, 2008). Their many unique properties have resulted in their development and synthesis for both industrial and technological applications, for instance; their large surface area makes them highly effective for catalytic purposes and drug loading, their pore structure makes them important as excellent adsorbent (Yang et al., 2003).Examples of xerogels include silica gel.

Xerogel is prepared by the sol-gel method, In the sol-gel method for the preparation of silica is removed from residual ash in the form of sodium silicate, and in a later stage of the process, treatment with acid converts the silica into a gel (Samantha et al., 2011). Therefore silica as an alternative material can be synthesized from inexpensive materials such as bottom ash. Other materials that can be easily used as a source of silica include bagasse ash, coconut husk, rice husk, clay, sand, etc.

Bottom ash is considered as a waste material in Reppie Waste to Energy Company, 250-240kg/ton day amount of bottom ash generates from 1400ton/day waste to energy production (Massreshaw. A, 2018). (Aneeta.M et al., 2018) studies of municipal solid waste incinerated the major chemical components of the bottom ash are CaO, SiO_2, and Al_2O_3, which is illustrated in the Ca-Si-Al ternary. Therefore, it is interested to prepare a higher value product such as silica xerogel from bottom ash.

1.2 Statement of the problem

In Ethiopia most of the textile industries are located near freshwater bodies.Most the factories have a lack of effluent treatment plants due to these pollutants discharge into the environment. Since most of them use Methylene blue for dying processes, because this dye has several advantages such as the price is relatively cheap, easy to obtain, good solubility and it is a basic dye. (Gong J.et.al., 2015) In the coloring process, 5% of methylene blue is bonded while the remaining 95% is wasted as waste, so this discharged waste creates an environmental problem in

the aquatic environment, the presence of dye in water systems limits the diffusion of sunlight through the water bodies and thus prevents photosynthesis in aquatic plants, impedes the growth of bacterial and causes a harmful effect to humans such as skin irritation, mutation, allergic, dermatitis, and cancer. Therefore to reduce the environmental impact of methylene blue by using silica xerogel adsorbent,which is preferable adsorbent because,it was obtained from high stabilitiy supply and inexpensive material of municipal solid waste bottom ash.

1.3 Objective

1.3.1 General objective

The general objective of the study, synthesis of silica xerogel from bottom ash of Reppi waste to energy as a Methylene blue adsorbent from textile wastewater.

1.3.2 Specific objectives

- ✓ Characterizing the physico-chemical properties of bottom ash collected.
- ✓ Synthesiing a silica gel from the bottom ash by sol-gel method.
- ✓ Investigating and statistically optimizing the selected synthesis parameter such as sodium hydroxide concentration, volume of sodium hydroxide to mass of bottom ash ratio and time on silica-gel purity.
- ✓ Characterizing a silica gel by FTIR and BET.
- ✓ Investigating and statistically optimizing methylene blue removal efficiency of the prepared silica-gel at different operational conditions such as methylene blue initial concentration, silica dosage and contact time parameter.
- ✓ Validating the optimum condition ,it performed on real textile dye house waste water

1.4 Significance of the study

The application of this study can be applied for both generating knowledge and solving the current problems which is currently prevailing on the removing of methylene blue dye from textile waste water It is paramount important in investigating xerogel and brings a great opportunity that brings strategic solution for industrial application. The production of xerogel from inexpensive municipal solid waste bottom ash is cost effective and environmentally conscious.

The replacing silica xerogel derived from bottom ash produced a lot of benefits for the environmental aspects, such as waste utilization give a solution towards final product quality by using low cost adsorbents to make safe environment.

In general, silica xerogel production from municipal solid waste bottom ash has a lot of benefits such as:

- ✓ It provides safety environment to the people, animals and plants.
- ✓ Produce low adsorbent from low cost material which is available locally.
- ✓ Give a solution towards final product quality by using low cost adsorbents to make safe environment.
- ✓ Provide further research area in waste management.

1.5 Scope of the study

This study deals with synthesis of silica gel up to used as an adsorbent for methylene blue dye from textile waste. The first stage is the conversion of municipal bottom ash MBA to silica xerogel by using different parameters; select the optimum condition based on quality of adsorbent and characterized the produced silica gel by physical and chemical properties. Finally by taking factors that can affect removal process, investigate optimum parameter for better MB removal efficiency.

Chapter Two

Literature Review

2.1 Dyes

All dyes are organic aromatic compounds with a conjugated double bond system, to which chromophores and auxochromes are attached. These functional groups reduce the number of conjugated double bonds needed for light absorption and result in molecules that are small enough to diffuse into fibers. Chromophores (Rivlin. J 1992) are unsaturated functional groups. Alone, they absorb visible or near-ultraviolet radiation. In a dye molecule, they function as electron acceptors. Auxochromes (Fessenden RJ and Fessenden JS., 1990) are saturated, functional groups. Auxochromes act as electron donors because the atom attached to the conjugated system has nonbonding electrons. Dye chromogens can be described as electron acceptor(s) (chromophores) interacting with an electron donor(s) (auxochromes) through a conjugated double bond system. The color of a compound depends on the wavelength of light that it absorbs. If a compound does not absorb any visible light it will be colorless. If a compound absorbs light we will perceive the complementary color, because the light which reaches our eyes is missing the wavelengths which have been absorbed. The ability of a dye to absorb light depends on the presence of certain kinds of structural features called chromophores. There are more than 100,000 commercially available dyes and more than $7x10^5$tones per year are produced annually (A. Kumar et al 2011; S.Patil et al 2011)

2.2 Dyeing process in textile industries

Dyeing is the application of color to the whole body of textile material with some degree of Colorfastness. Textiles are dyed using continuous and batch processes and dyeing may take place at any of several stages in the manufacturing process (i.e., before fiber extrusion, the fiber in staple form, yarn, fabric, garment). Most textile dyeing is done in the finishing departments of basic textile manufacturing facilities, although there are also several commission dye houses. From an environmental perspective, dyeing has typically been viewed as a wastewater issue due to the large quantities of water, chemicals, and auxiliaries (such as salt) includes a depiction of a typical fabric dyeing operation (USEPA, July 1998)

Dyeing is complicated by the fact that there are many sources of color variations, such as dyes, substrate, and reparation of the substrate, dyeing auxiliaries (such as salt) used, and water. Processing variables such as time, temperature, and dye liquor ratio (pounds of dye bath to pounds of cloth) also affect dyeing results (USEPA, July 1998). The Main pollution in textile industries came from the dyeing section. These processes require a wide range of input chemicals and dyestuff, which is generally an organic compound of complex structures (A. Kumar et al., 2011). These can be classified both by their chemical structure and their application to the fiber type. Dyes may also be classified based on their solubility: soluble dyes which include acid, mordant, metal complex, direct, basic, and reactive dyes; and insoluble dyes including azoic, sulfur, vat, and disperse dyes (Haimanot .M, July 2007). Since this research is concerned with basic/cationic dye (methylene blue), it is one of the common micropollutants to the environment.

Micropollutants are highly water-soluble, often charged, organic molecules that are increasingly found in ground and surface water (A. Alsbaiee et al.,2016). These organic molecules mainly come from the chemical and pharmaceutical industries. Among the leading sources for micropollutants, industrial use of synthetic dyes has increased considerably over the last few decades, particularly in textiles, plastics, and papers (M. Ib´anez et al., 2017). The textile industry is the most prominent where effluents containing large amounts of dye residue have to be treated before being discharged into wastewater streams. If not done properly, water pollution with toxic dyes, metal ions, and organic contaminants pose serious environmental hazards, especially for aquatic biosystems, where symbiotic processes are affected by the contaminant induced inhibition of the photosynthetic activity (C. J. Madadrang et al., 2012). Although safety protocols are in place for newly discovered molecules and their environmental fate, there are still many unknowns, especially if they undergo chemical transformations like oxidation. Conventional sorbents like activated carbon suffer from low kinetics and specificity when it comes to extremely hydrophilic micropollutants (J. Byun et al., 2016).

2.3 Methylene Blue

Methylene blue is a heterocyclic aromatic compound with molecular formula $C_{16}H_{18}ClN_3S$ as shown in Figure 2.1, with IUPAC name **3,7-bis(Dimithylamin)-phenothiazine-5-ium chloride.**

Methylene blue (MB) is a cationic thiazine dye that is deep blue in the oxidized state while it is colorless in its reduced form leucomethylene blue (Miclescu A. and Wiklund L. 2010) . MB leading to its high thermal, light stability, and poor biodegradability. It is difficult to degrade in the environment. MB can harm humans, wildlife, and microorganisms. Chemical and physical properties of Methylene blue is summarized in Table 2.1 (Tani A., Thomson A. and Butt J., 2001).

Table 2.1 chemical and physical property of methylene blue(MB)

Properties	**Values**
Chemical formula	$C_{16}H_{18}CIN_3S$
Color absorbance(λ_{max})	665
Solubility in water	35.5g/l
Molecular weight	319.09g/mol
Melting point	180^0c
Boiling point	No data

Source: Tani A., Thomson A. and Butt J.,2001

2.3.1 Importance of Methylene blue

Methylene blue ($C_{16}H_{18}N_3SCI$) is a dye used by manufacturing processes such as; rubber, textile, cosmetic, plastic, printing, etc. in the textile industry methylene blue (MB) is one of the most commonly used substances for dyeing cotton, wool, and silk. Medicinal use of MB include therapeutically in the treatment of methemoglobinemia and cyanide poisoning. Other medicinal uses of methylene blue include the management of chronic urolithiasis and treatment of cutaneous viral infections as well as the treatment of manic-depressive psychosis.

2.3.2 Impact of Methylene Blue dye on human and animals

- ✓ **Impact of Methylene Blue dye on human**

MB can harm humans, wildlife, and microorganisms. Acute exposure to methylene blue has been found to cause increased heart rate, cyanosis, vomiting, shock, Heinz body formation, jaundice, quadriplegia and tissue necrosis in humans. In addition, corneal and conjunctival injury has been reported following acute exposure to this compound. Intravenous administration of methylene

blue has been found to cause bluish discoloration of the urine and stool. Numerous case reports were found in the literature describing the effects of methylene blue on the newborn, following the injection of this compound into the amniotic fluid before delivery. At birth, many of the infants reportedly had deep blue stained skin and voided blue urine. Other symptoms including respiratory distress, hyperbilirubinemia, methemoglobinemia, Heinz body formation and increased heart rate occurred after birth. No data were found on the prechronic effects of methylene blue in humans. Chronic application of methylene blue-containing eye drops has been found to result in staining of the bulbar and palpebral conjunctiva, the lid margins and slight staining of the corneal epithilium. No other data were found on the chronic/carcinogenic effects of methylene blue in humans. Methylene blue has been found to cause an elevation in follicle stimulating hormone and estradiol in fallopian tube secretions, and uterine and peritoneal fluids in vitro. In addition, methylene blue was found to significantly inhibit sperm motility in vitro in samples prepared from human semen. No other studies were found on the reproductive effects of methylene blue in humans. (Arthur D. Little 1990).

- ✓ **Impact of Methylene Blue dye on animals**

Numerous reports were found in the literature describing the association between methylene blue and the formation of Heinz bodies in animals. Intraperitoneal administration of methylene blue has been found to induce Heinz body formation in cats, dogs, mice and rabbits. In cats, methylene blue was observed to cause bluish stained skin, anemia, discolored urine, dyspnea, depression, respiratory stimulation and increased blood pressure. In addition, methylene blue has been found to cause corneal and conjunctival injury in rabbits. No data were available on the prechronic, effects of methylene blue in animals. Administration of this compound at a concentration of 4% in the diet for 2 years was not found to induce tumor formation. Methylene blue has been found to inhibit the ability of mouse embryos to grow and cleave in vitro. This compound also caused an increase in implantations and resorptions in litters born to rats fed diet containing methylene blue.

2.4 Textile dyeing effluent

The large quantities of water are needed for textile processing, dyeing and printing. Among these various processes, dyeing process includes fixing dyes on fabrics, washing etc requires more

water and it consumes 16% of total water usage depending on the type of dyes used and this dyeing sector contributes to 15% - 20% of the total waste water flow. According to WHO nearly 80% of water is polluted in developing country due to the dumping of domestic waste into aquatic bodies.

Approximately calculating that 80,000 tons of dyes used in various industries such as food processing industries, cosmetics, paper mills etc but the textile division alone consumes about 60% of total dye production for coloring a variety of fabrics and about 10–15% of unspent dyes are let out into the clean water bodies which makes the water highly coloured and polluted, typically with a concentration range 10–200 mg/L.

Major pollutants in textile wastewaters are high suspended solids, chemical oxygen demand,heat, color, acidity, and other soluble substances (Khandaker Rashedul,2008).COD values of composite wastewater are extremely high compare to other parameter. In most cases BOD/COD ratio of the composite textile wastewater is around 0.25 that implies that the wastewater contains large amount of non biodegradable organic matter (Khandaker Rashedul,2008).Besides the parameters and values mentioned in the table 2.2

many discharge standards doesn’t allow visible color in the wastewater at all (Khandaker Rashedul,2008).As a result of all these problems treating the wastewater before discharge is becoming mandatory.

Table 2.2: Limit values for discharge to in land water

Parameter	Limit values
Temperature	40^{o}C
BOD5 at 20^{o}C	6-9
Total nitrogen (as N)	50 mg/L
COD (mg O_2/l)	40 mg/L
Total phosphorous (as P)	150 mg/L
Suspended solids	10 mg/L
Total ammonia (as N)	30 mg/L
Oil, fats and grease	20mg/L
Phenols	1mg/L
Mercury (as Hg)	0.001mg/L
Nickel (as Ni)	2mg/L
Cobalt (as Co)	1mg/L
Lead (as Pb)	0.5mg/L
Antimony (as Sb)	2 mg/L
Tin (as Sn)	5mg/L
Chromium (as Cr VI)	0.1mg/L
Chromium (as total Cr)	1mg/L
Arsenic (as As)	0.25mg/L
Cadmium (as Cd)	1mg/L
Zinc (as Zn)	5mg/L
Copper (as Cu)	2mg/L
Mineral oils (Interceptors)	20mg/L
Benzene, toluene and xylene (combined)	1mg/L
Mineral oils (Biological Treatment)	5mg/L
Organochlorine pesticides (as Cl)	0.03mg/L
Organophosphorous pesticides (as P)	0.003mg/L
Adsorbable organic halogen compounds(AOX)	5mg/L
Sulfides (as S)	2mg/L

*Source :*Environmental protection authority (EPA) 2004

2.5 Overview of decolorizing wastewater in textile industries

Wastewater containing dyes are very difficult to treat since the dyes are recalcitrant organic molecules, resistant to biological degradation, and are stable to light. There are different methods for the removal of textile effluents. The technologies for color removal can be divided into three major categories: biological, chemical, and physical processes (Robinson.T *et al*.,2001). All of them have advantages and drawbacks. Because of the high cost and disposal problems, many of these conventional methods for treating dyes wastewater have not been widely applied on a large

scale in the textile and paper industries (Banat.IM *et al.,* 1996). Discharge standards will undoubtedly restrict color to a maximum value of 100 mg Pt. Co/L (Marmagne.O *et al.* ,1996). But the results of the conventional treatments are far from complying with this level. The Provisional Environmental Standard for Ethiopia, proposed by the Environmental Protection Authority (EPA) sets emission limits of 5 mg/L of adsorbable organic halogenated compounds. To become the more familiar with the behavior of organic dyes to determine the dye removal technology that best meets the needs and economy of each user company.

2.5.1Biological treatment

The conventional biological treatment is the most economically used methods compared to other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants (Mc.Mullan *et al.,* 2001). However, their application is often restricted because of technical constraints. Biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation (Bhattacharyya, *et al.,* 2003). Biological treatment is incapable of obtaining satisfactory color elimination for concentrated wastes, this is due to their complex chemical structure and xenobiotic nature (H.S Ashoka, and S.S.Inamdar; Kunwar *et al.,* 2003).

2.5.2 Chemical processes

The most frequently used waste treatment method is a chemical process such as coagulation, Fenton's process, combined with floatation and filtration, precipitation-flocculation with Fe_2+/$Ca(OH)_2$, electro floatation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. But, chemical techniques are often expensive, and although the dyes are removed, the accumulation of concentrated sludge creates further disposal problems (Y.C.Sharma *et al.,* 2011).

2.5.3 Physical processes

Different physical treatment techniques are also successfully tested, such as membrane-filtration processes(nano filtration, reverse osmosis, electro dialysis) and adsorption techniques.

Nowadays; adsorption is the most preferred technique because it removes the dye and also creates a platform for dye recovery and reuse. Other advantages of adsorption are the possibility to regenerate the adsorbent, adsorbate recovery, and the operation that generates no sludge (A.S. Kovo *et a., 2018).*

2.6 Adsorption fundamentals

Adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency in the removal of pollutants that are not easily biodegradable. Adsorption can produce high-quality water while also being an economically feasible process (K.K.H. Choy *et al.,* 1999). Decolorization is a result of two mechanisms - adsorption and ion exchange (Y.M.Slokar and M. Le Marechal, 1998) and is influenced by many factors including dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time. The most used adsorbent is activated carbon, and also other synthetic adsorbents like silica xerogel.

Different types of adsorbents used for color removal used; adsorbents are classified into natural adsorbents and synthetic adsorbents. Natural adsorbents include charcoal, clays, clay minerals, zeolites, and ores. Synthetic adsorbents prepared from agricultural products and wastes, household wastes, industrial wastes, sewage sludge, and polymeric adsorbents. Each adsorbent has its characteristics such as porosity, pore structure, and nature of its adsorbing surfaces. Many waste materials include fruit wastes, coconut shell, scrap tire, bark and other tannin-rich materials, sawdust, rice husk, petroleum wastes, fertilizer wastes, bottom ash, sugar industry wastes blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss and, etc (Rashed N., 2013). Adsorbents are also used for removal of dye and organic colored matter from textile effluents (i.e. removal of 40-90% basic dyes and 40% direct, with maximum adsorption capacities for basic dyes of 338mg/g.

The adsorption of basic dye (MB) onto the prepared silica gel adsorbents from bottom ash was investigated. Bach isotherm studies were carried out under varying experimental conditions of contact time, temperature, and pH. The study results indicated that the prepared adsorbents from bottom ash could be substitution ally used for the adsorption of basic dye as compared with the silica gel. The adsorption isotherm describes the relationship between adsorption capacity and

the concentration of adsorbate at a constant temperature. When the temperature decreases the free energy (Gibbs, enthalpy changes, and entropy changes) becomes negative (Lukluil Maknun et al 2018).

Most adsorbents are highly porous materials because the pores are generally very small, the internal surface area is in the order of magnitude greater than the external area. In this study, the synthetic adsorbent is used as adsorbent because, most of the raw materials for synthesizing synthetic adsorbents were obtained from wastes materials that have an environmental impact rather than natural adsorbents, due to this reason to reduce environmental pollution by utilizing wastes as an adsorbent source for removing MB from wastewater. Therefore, this study silica gel prepared from BA. Adsorption of MB by adsorbents is advantageous over the other methods, due to its simplicity, low cost (L.Fan *et al*.,2013).

Based on (M. Najaf *et al.*,2011) studies mesoporous SiO_2 adsorbent has been used to purify MB contaminated wastewater. According to (Qadeer A *et al.,2019*) studies, silica has a large surface area and has good porosity rather than other adsorbents. This silica gel is an example of "hydrophilic"; adsorbents of this type (Suzuki, 1990).

2.7 Silica xerogel

Silica gel is properly called silica xerogel; it is one of the synthetic adsorbents obtained from silica that is the most abundant and most complex material in the world. They have been used extensively as catalysts and for adsorbing organic compounds and removing heavy metals from wastewater because porous silica materials have large specific surface areas, controllable narrow pore size distribution, and high adsorption capacities (W. Xie *et al*., 2015). Xerogel generally possess the properties of higher porosity and larger surface area together with very smaller pore sizes. Silica gel is a controlled dehydrated polymeric structure made from the coagulation of a colloidal solution of silicic acid with the formula SiO_2nH_2O.

Silica gel has shown good performance in the treatment of wastewater. It is a chemically inert, non-toxic material composed of amorphous silicon dioxide. It is a highly porous structure, characterized by uniformity of the arrangement of the pores and their sizes. The pore area of silica gel varies with the method of synthesis (Hafiz *et al.*, 2009).

Table 2.3 Typical characteristics of silica gel

Particles density	0.7-1g/cm3
Total porosity	0.5-0.65
Pore volume	0.45-1cm^3/g
Specific surface area	700-800m^2/g
Range of pore radial	1-12

Source: Do.oscar, 1988

2.7.1 Pore structure

The word pore comes from the Greek word, meaning a passage (Marsh, 1989). In this sense, a pore is a class of void which is connected to the external surface of a solid and will allow the passage of fluids into, out of, or through a material. Marsh‘s (1989) claim that, in the scientific literature on porous solids the terms _open pore‘ and _closed pore‘ are used, the former a pore which is not so connected.

Differences in pore sizes affect the capacity for molecules of different shapes and sizes, and this is one of the criteria by which xerogels are selected for a specific application. Porosity is classified by IUPAC into three different groups of pore sizes.

- ✓ Macropores (above 50nm diameter)
- ✓ Mesopores (2-50 nm diameter)
- ✓ Micropores (Under 2 nm diameter)

The pore structure of amorphous silica strongly affects the properties and functionality of silica and, therefore, its possible applications. For instance, the pore structure plays afundamental role in catalysis, drug delivery and ultrafiltration (A.Lazaro *et al.*, 2018).

Based on (Farnaz Ghajeri., 2019) study Mesoporous silica materials are used as adsorbents, catalysts, etc., in applications . The structure of mesoporous silica is not ordered and has a wide variety of pores size and shape in the structure. Having bigger pores than microporous zeolites,both the internal and external structure of mesoporous silica can be functionalized.The basis for the synthesis of mesoporous silica is hydrolysis and condensation of the silica source.

It can be synthesized in both basic or acidic conditionand usually a surfactant is used to produce the mesoporous structure.

2.7.2 Synthesize of Xerogel

There are several methods to synthesize silica gels these are the St¨ober method and sol-gel method. However, the Stober method has to use a high-cost alkoxide or organ metallic compound and is also only used to control the perfect particle size of colloids or pore size of mesostructure material due to high production cost (Sang-wook Ui *et al.*,2014 and A.Lazaro *et al.*,2018). Therefore, in this study, a sol-gel method was demonstrated. The term "sol" is intended to encompass any suspension of fine silica particles in an aqueous media. The term "gel" is intended to encompass a three-dimensional network formed by silica particles, in either wet or dry form due to the reaction of sodium silicate and sulfuric acid.

(Sang-wook Ui *et al.*,2014) The sol-gel method obtains a high purity silica powder; however, the process yields a low percentage. In sol-gel mainly two types of silica sources were used to synthesize this porous silica, that is, tetraethyl orthosilicate (TEOS) and sodium silicate solution (Liping Sheng *et al.*,2017). However, these raw materials are expensive, especially the TEOS is more expensive than sodium silicate due to this the cost of adsorbent silica materials increase. Therefore, substitute silica sources must be found. Municipal bottom ash contains a large amount of silicon oxide, which can be used as the raw material for synthesizing silica gel materials. In this study, sodium silicate is derived from bottom ash by using sodium hydroxide (NaOH) as an extraction solvent. Sodium silicate solution was selected due to the cost of synthesizing silica.

The Xerogel can be prepared in two steps; Solution-sol-gel or sol-gel (for short) processing starts with a solution or a sol which becomes a gel. The solution can be prepared from either inorganic salts or organic compounds which then are hydrolyzed and condensed to make a sol or a gel. According to (K.ishizaki et al,1998) One can stop at the sol stage which refers to a dispersion of particles of colloidal dimensions in a liquid or proceed to the gel state which refers to a three-dimensionally-linked solid network with liquid filling the pores.

Colloidal Stability in the colloidal state means that colloidal particles do not settle in a short time or bunch up to form a larger cluster and then settle after a short period (Everett, D. H. 1971). In this case, colloidal silica is easy to link together with other particles by aggregation, coagulation, flocculation, gelation, etc. If particles link together to form larger clusters or three-dimensional

networks and start to settle down in the liquid phase, even become gel form, it means that silica sols have lost their stability.

Even though both gelation and coagulation will make silica sols lose their stability, they are different from each other. When a sol is gelling, colloidal silica particles link with each other one by one and form long chains. As a result, sol will become more viscous and finally look like soft solid materials. On the other side, coagulation somehow means that precipitation. Silica particles will link with each other and form clusters. When clusters become large enough, they will settle down, so that sediments in the liquid phase can be seen at the bottom of containers. Fig 2.1 (Iler, R. K. 1979) Shows the difference between a sol, gel, and precipitate of silica.

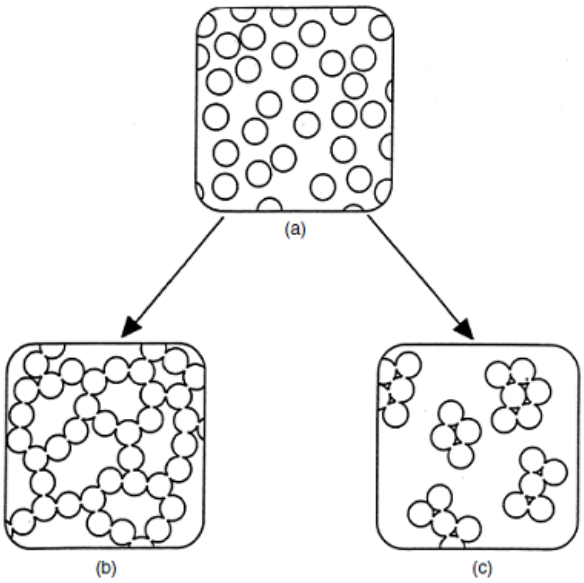

Figure 2. 1: Silica gel versus precipitate: (a) sol, (b) gel, and (c) flocculation and precipitation

Source; (Iler, R. K. 1979)

- ✓ **Extraction of sodium silicate**

Silica is extracted from municipal bottom ash by sodium hydroxide (NaOH) in the form of sodium silicate. Based on previous studies (Kalapathy *et al*, 1999; 2000; 2002), the amorphous silica has increase solubility in solution with pH values higher than 10.therefore; the amorphous

silica production from the bottom ash by sodium hydroxide solution that has a pH value greater than 10.

- ✓ **Sol-gel process**

Extracted sodium silicate solution serves as precursors in the preparation of gels. Most commonly silica gels are manufactured by acidifying an aqueous solution of sodium silicate. According to (Hafiz et al, 2009) studies the material that first forms is called a hydrosol, the particles of which agglomerate and results in the growth of silica polymers. One can stop at the sol stage which refers to a dispersion of particles of colloidal dimensions in a liquid. The hydrosol is typically formed at low pH and if the subsequent washing steps are also conducted at relatively low pH, the final product then has a high surface area. When hydrosol ceases to flow like a liquid (the gel time), it is termed hydrogel.

The process of transforming a liquid sol into a gel state with subsequent post-treatment (washing) which have an advantage to produces a uniform structure with high purity gel obtained at room temperatures (Gunvant H et al 2018).

Interaction of acid with sodium silicate solution produces orthosilicic acid which is an intermediate product of hydrolysis. It is a very unstable substance that readily condenses with it to give a colloidal polymer of silica sol (Hafiz et al, 2009).

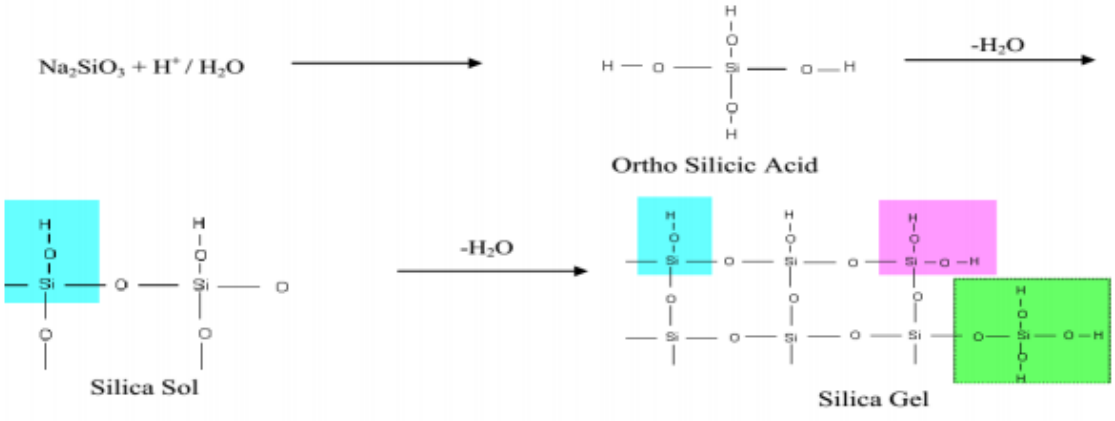

Fig 2.2 Different forms of hydroxyl group that can occur on the surface of Silica Gel

Source: Hafiz, 2001

Further condensation of silica sol takes place on standing which assumes the form of a gel. Silica gel is a continuous three-dimensional network of spherical particles of colloidal silica. Both siloxane (-Si-O-Si-) and silanol (-Si-OH) bonds are present in the gel structure. The pores of the gels are interconnected and filled with water from hydrolysis and condensation reactions.

The silanol groups in turn may condense to form siloxane bridges (-Si-O-Si-). Therefore, the surface composition of silica gel Fig. 2.3 is made up of physically adsorbed water, chemically bound water, and silicon dioxide (J. Bouaziz, B. Elleuch, R. Garbi, J. Soc. Chim. de Tunisie 3).

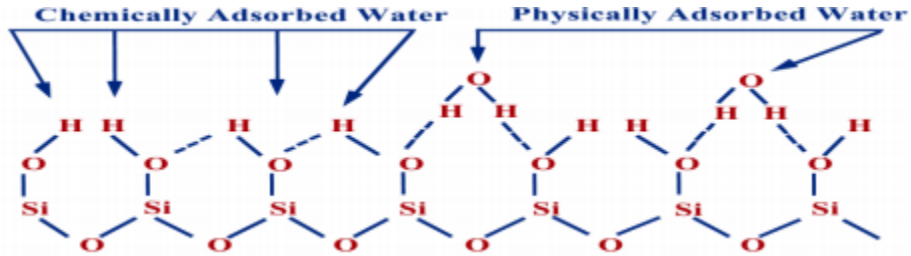

Fig 2.3 Silica gel surface showing physically and chemically adsorbed water

The rate of gelation of silica sol is greatly influenced by the amount of water present, the pH of the sol, and the temperature of the contents. The characteristic of silica gel is to shrink on standing during which process known as syneresis, a liquid phase (water) is squeezed out of the gel. Further removal of water by evaporation produces different grades of silica gel depending upon the number of hydroxyl groups left or removed after dehydration. A typical good quality adsorbent silica gel has residual water contents of about 6 %, is hydrophilic, and has a surface area of 200-800 m^2 /g (Kirk Othmer, 1997).

2.7.3 Factors affecting synthesize of silica xerogel

- ✓ **Raw material**

The major inherent ash forming elements in biomass include Ca, Si, Al, Ti, Fe, Mg, Na, K, S, and P. The composition of ash affects its behavior under high temperatures of combustion and gasification reactors, due to this raw material have an impact on the properties of silica gel product, Pore structure, Purity and yield of the end product. Since a silica gel is a structurally amorphous material, almost any silicon contain solid material can be converted into silica gel (F. Rodriguez-Reinoso, 1997). There are previous studies relating to this, silica gel with high surface

area and pore volume can be produced from a large amount of silicon-containing raw materials like agricultural waste which include rice husk, coal, cane bagasse, peanut shell, and other by-products due to low cost of production scraps (Kirk- Othmer,1964). In the selection of raw material for the preparation of porous silica gel, several factors are taken into consideration.

The factors are:

- ✓ High silica(SiO_2) content
- ✓ Low heavy metals content
- ✓ Low density and sufficient content
- ✓ The stability of supply in the countries
- ✓ Potential extent for extraction
- ✓ Inexpensive material

According to the above factors, Bottom ash (BA) is originating from municipal solid waste incineration (MSWI) which is a silica-rich residue, it can be a good candidate for the synthesis of sodium silicate due to its high silica content and easy availability (Qadeer.A *et al*., 2018).

According to the International Ash Working Group (IAWG), the ash or residue from the incinerator is named based on the point of collection of the ash. Large volumes of the total residues are composed of bottom ashes (more than 90%), and these contain the least salts, and least heavy metals therefore best suited to recycled material. Only 1–3% is fly ashes, and these are rich in chlorides, sulfates, and other heavy metals, making them less suitable to be recycled.

Bottom ash for synthesizing of silica gel,(Liu et al., 2014) study results show that municipal ash contains more than 50% silica and the silica has an amorphous phase, low density, and the stability of supply in the countries better than those materials for the manufacture of silica gel.

In Table 2.4 the bulk chemical composition of BA is provided showing that SiO_2 is the major constituent of the ash, comprising up to 53.8wt %. In addition to other major oxides, BA contains a range of potentially leachable elements: Ti, Zn, Cu, Ba, Pb, Cr, and Mn. (Q. Alam et al.,2019) The crystalline phases in bottom ash (BA) can be categorized into three groups: 1) silicates: albite, diopside, melilite, and quartz, 2) carbonates: calcite and dolomite, and 3) iron oxides: magnetite and hematite. Overall, only 19wt % of the ash consist of crystalline phases, and the rest (81 wt %) is amorphous. The presence of high amorphous content and silicate minerals

makes this fraction of BA ideal for the extraction of silica. Under alkaline conditions, the dissolution of the amorphous content and soluble silicate phase such as melilite is expected. The contribution of other well crystalline silicate phases (quartz, albite, and diopside) towards the soluble silica is considered negligible due to their much lower solubility.

Table 2.4 Chemical Composition of MSW Bottom ash

Compounds	**Content(wt%)**
SiO_2	53.8
CaO	18.3
Al_2O_3	7.5
Fe_2O_3	3.3
NaCl	4
K_2O	2
MgO	1.2
ZnO	1
CuO	4
TiO_2	1.1

source: Z.-S. Liu et al. 2014

- ✓ **The Particle size of BA**

The motivating factor in choosing a silicate source for mesophase synthesis has been the primary particle size as this affects silicate dissolution. Provided the particles were extremely small and dissolved in water, as in the hydrolyzed state, the silicate source will be irrelevant. (A.lazaro *et al.*,2018) concluded that the specific surface area (SSA) silica gel was mainly influenced by the size of the primary particles therefore, the primary particle size remained constant.

The size of the material has affected the yield of sodium silicate during the extraction this is due to the availability of heavy metals. since the existence of heavy metals in the bottom, ash is also dependent on the size of the particles. A size distribution analysis of heavy metals in bottom ash performed by Chen et al. in 2008 concluded that about 20-40% (w/w) of heavy metals were found in fine particles (< 0.21 mm), about 30-40% of heavy metals showed up in medium particles (0.21 to 2.36 mm) and the remaining 30-50% of heavy metals were located in coarse

particles (larger than 2.36 mm). if the bottom ash contains a high amount of impurities such as Fe, Ca, K, and S, these did not dissolve to any significant amount and thus the imperfect mesoporous material could not be attributed to the impurities. According to Eurostat data fine bottom ash particle size, 0.075mm /75 µm/NO 200 mesh .therfore silica were obtained from on this point on bottom ash. (Jayhyun Park et al.,2012) only amorphous silica with fine particle size is easier to dissolve in NaOH.

It is also found that the metallic element such as Copper(Cu), Nickel(Ni), Chromium(Cr), Zinc(Zn), and Lead(Pb) in fine bottom ash particles, the existence of those elements in the ash could pollute the environment and pose a danger to public health (A. A. Kadirand *et al.*,2016) therefore, an effective treatment need to be done to overcome the problem. Leaching treatment shows a potential route in silica extraction and reducing heavy metal compounds. From previous research, strong acids such as sulphuric acid (H_2SO_4), hydrochloric acid (HCl), and nitric acid (HNO_3) solution were used conventionally in leaching treatment in the extraction of silica material (C.P. Faizul *et al.*, 2014).

In the leaching process, there are three important parameters which are temperature, contact time, and selection of solvent. To obtain an optimized solubility and mass transfer, the temperature was adjusted accordingly. There are two categories in leaching which are percolation and solid dispersed. Usually, the solid was crushed into small pieces which are an average particle size of 75 µm before treating ash (Ahmad Asyari Yahya 2017). (Q. Alam et al 2019) The Leaching treatment of municipal solid waste BA shows a potential route in silica extraction and reducing heavy metal compounds, In the presence of 1N hydrochloric acid A ratio of 1: 3 (wt: vol) between BA and hydrochloric acid was used and the mixture was stirred slowly for 24 h at 20^0C.

- ✓ **Temperature**

Temperature affects the extraction efficiency that is soluble silica content in sodium silicate solution. According to (Q.Alam *et al.*, 2019) study result shows that 75^oc is the optimum temperature to obtain the better amount of soluble silica content during the extraction process. When the temperature increase there is no significant difference between silica content in extracted sodium silicate solution and also when the temperature decrease 20% of the available

silica was dissolved at 20^{o}C during the first 24 hr, it needs much time to increase dissolved silica content.

Temperature affects the reaction of hydrochloric acid with sodium silicate during this reaction, the favorable temperature was found by (Hafiz *et al.,* 2009; Samantha *et al*., 2011) which is at room temperature is to produce a good quality product. As reported by several authors, temperature significantly affects the production yield of silica gel and also the quality of silica gel.

According to (Zhen-Shu Liu *et al.,* 2014) study shows The filtered solid (gel) was dried overnight in an oven at 105^{o}C to remove the water and then placed in a high-temperature furnace at 550^{o}C for 6 hr for calcinations of the filtered solid yielded mesoporous silica by removing organic compounds and surfactants which affects the purity of silica gel for adsorption capacity.

- ✓ **Time**

Reaction time has a greater impact on the extraction of silica. From a previous study, the extraction times normally used were from 1hr to 3 hr for bagasse bottom ash (Lukluil .M *et al*., 2018) and clay (Samantha *et al*., 2011 and Ayegba C. O, 2015). As time increased, the percentage of yield decreased gradually and the surface area also increased, This result is possibly due to the raw material composition, which results in the formation of silica gel.

From (N.-u. Amin et al. 2016) studies the reaction time of 30 and 45 min, no silica extraction was observed even the acid and base concentration was kept and therefore the extraction time should be above 45 min.

- ✓ **Solvent concentration**

(N.-u. Amin et al.2016) studies, the concentration of sodium hydroxide (NaOH) affects the extraction of silica. The amount of silica increases with the increase in the concentration of alkali 1M up to 3M. Above this concentration, a slight decrease in the amount of extracted silica was observed. The increase in silica with the concentration of base is attributed to the completion of stoichiometric ratio during the reaction and also the extraction of silica by less than 1M concentration of sodium hydroxide (NaOH) the amount of extracted silica decrease (N.-u. Amin et al.2016). Amorphous silica is capable of forming sufficient silanolates for the subsequent

micelle formation at solid-liquid ratios greater than 0.25. The concentration of sodium silicate affects characteristics of purity, bulk density, and yield of silica gel(Hafiz, 2001).

The concentration of HCl has an effect during, the silica gel formation; no silica precipitate is formed on the extracted silica with 1 and 1.5 N HCl, and above this concentration, silica precipitate started. Maximum silica precipitated is observed with 2.5 N HCl above which slight decrease in silica. The decrease in silica above 2.5 N may be the re-dissolution of silica in a highly acidic environment (N.-u. Amin et al.2016).

- ✓ **Salt effect**

The dehydration reaction of silicic acid will happen in the alkali solution (Horacio E. Bergna, William and O. Roberts. 2006) In this case, silica forms nuclei first and thus particle grows further. Therefore, increasing salt concentration means increasing sodium ion concentration, resulting in a larger particle size of produced silica. However, during the synthesis of the silica powder, the remaining Na+ in sodium silicate affects the network therefore it was removed through the sol-gel process. According to (Y. Arai *et al.*, 2004 and A. Borisov *et al.*, 2006) studies in the silica sol, the Na+ ion was breaking the silica network structures as a modifier during silica sol-gel gelation and decreasing the purity of silica powders. To remove the sodium from sodium silicate, sodium silicate was mixed with HCl acid. Silica hydrogel was made by the sol-gel reaction after the sodium ions were removed by washing until the pH becomes 7. (K. M. Davis and M. Tomozawa., 1995 and M. Tomozawa *et al.*, 2001) There are two washing methods: deionized water washed on a filter paper and a centrifugation method. Compared to the XRD data, the filter paper was better for the removal of Na+ ions to produce a more high purity silica powder product; however, the main drawback is the loss of silica.

- ✓ **pH**

The pH has a great effect on not only porosity but also the particle size of silica particles. Tzong – HorngLiou found that pH strongly affects the surface area of silica particles. Surface area decreases with an increase of pH value, i.e. the silica obtained at pH 9 had the lowest surface area (237 m2/g), while the highest surface area (634 m2/g) was obtained at pH 3. When pH increases from 3 to 9, as shown in the following two paths, a condensation reaction may happen during gel formation, resulting in increased particle size and porosity.

$$(OH)_3Si+OH \longrightarrow (OH)_3Si - O- + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.1)$$

$$(OH)_3Si - OH + (OH)_3Si - O- \longrightarrow (OH)_3Si -O- Si(OH)_3 + OH\ldots\ldots\ldots \quad (2.2)$$

Where, the OH plays an important catalyst role. In the acid regime, reduced pH leads to changing of silanol bonding (Si - OH) to siloxane bonding (Si - O- Si) and gel formation is slow. As can be seen above, the OH increases the reaction of equation (2.1). In the acid solution, decreasing of OH will result in more silanol groups (Si - OH) change into siloxane linkages (Si - O- Si) so, that colloidal suspension becomes more stable. In the basic solution, the reaction will reverse so will siloxane change into silanol groups In this case; silica is composed of small particles and therefore, possesses a high surface area. In the basic regime, surface siloxane bonding tends to form silanol bonding. Siloxane linkages create negative charges and increased electrostatic repulsion between silica particles (J. Schlomach and M. Kind, J. 2004). The charge develops silica particles to connect, so that particle size becomes larger when pH increases. Therefore, low porosity and lower surface area will be obtained in this situation.

The quality of silica gel was greatly affected by changes in the pH level of the hydrosol, this may be due to the reason that pH 7 stabilized sol particles grew to gel (Hafiz *et al.*, 2009), while the low pH level (pH $\leq$ 2) of the hydrosol, the gelation can take several days, even several weeks for pH $\leq$ 2, whereas, for basic solutions, the gelling is instantaneous. The gelling time is a parameter that depends on pH and metasilicate solution concentration (M. Besbes *et al.*, 2009).

- ✓ **Mixing rate**

Preparation of silica gels as affected by mixing rate and it was observed in previous studies that the product quality, purity, and gel size were changed by changing the stirring rate. (Hafiz *et al.*, 2009 and Samantha *et al.*,2011) studies show that the addition of HCl was slowed down in sodium silicate solution, the reaction was completed in18-20 min, slow constant stirring was done to promote gel formation.

2.7.4 Properties of silica Xerogel for adsorbing methylene

Nanoporous materials are also used as adsorbents in purification applications, as the efficiency of the adsorbents depends on surface area, pore and particle size distribution as well as chemical structure, etc.

Characterization for silica gel (silica Xerogel) is very important in order to classified silica gel for specific uses. Basically, silica gel characterized by physical properties and chemical properties. As (Hafiz *et al.,* 2009) mentioned that the characteristics of silica gel depends on the physical properties of the raw materials as well as sol gel method used. Physical, chemical, and surface characteristics of silica gel determine its efficiency in removing the targeted methylene blue. Physical properties of silica gel, such as bulkdensity, Moisture absorptive capacity and moisture content can affect the use of a silica gel either suitable or unsuitable for specific applications.While the specific surface area of silica gel and surface chemistry is classified as chemical properties of silica gel.

2.7.5 Physical Properties of xerogel

- ✓ **Moisture content**

Silica gel is generally priced on a moisture free basis, although occasionally some moisture content is stipulated, e.g., 4, 5, 6%. Unless packaged in airtight containers, some silica gel when stored under humid conditions will adsorb considerable moisture over a period of month. They may adsorb as much as 5 to 6% moisture and still appear dry. For many purposes, this moisture content does not affect the adsorptive power, but obviously it dilutes the silica. Therefore, an additional weight of moist silica gel is needed to provide the required dry weight (Hafiz *et al.*, 2009).

- ✓ **Bulk density**

Density is particularly important in waste water decolorization of methylene blue. When the two silica gel are differing in bulk density are used at the same weight per liter, the silica gel having higher bulk density will be able to adsorbing more liquor volume before the available cake space is filled. Silca gel with an adequate density also help to improve the adsorbing rate .Generally, silica gel with a bulk density of about (0.7-1g/cm$^{3)}$is adequate for adsorption of methylene blue (Ayegba C. O et al,1985).

- ✓ **Particlesiz distribution**

As particle size increases the adsorption of dye decreases and hence the percentage removal of dye also decreases because,the available surface area decrase As silica gels are produced in large particle size ,the adsorption of dye dcrease.therefore silica grinding rather large granules, irregularly broken particles with a rather wide particle size distribution are obtained. the quality of the silica gel depends on a narrow particle size distribution. It is generally necessary to size the silica gel obtained by the grinding process,therefore the size of particle ≤ 100 μm it is better for adsorption of dye (Temechachew Tigabu., 2017).For larger particles, the diffusion resistance to mass transfer is high and most of the internal surface of the particle may not be utilized for adsorption as a result the amount of dye adsorbed is small.

2.7.6 Chemical properties of xerogel

- ✓ **Surface area**

Surface area is the single most important characteristic of silica gel designed for adsorption of Compounds from liquid media such as waste water (Weber and Vliet, 1980),because of its large surface area (200-800m^2), silica gel has a great ability to adsorb organic molecules from liquids or vapors (Roy, 1995). Large surface area is generally a requirement for a good adsorbent For adsorption of compounds from liquid media such as waste water, surface area is an important characteristic of an silica gel. Since silica gel has a large surface area due to having highest adsorptive porosity of any material known, it has a high capability of adsorbing organics such as colored materials from waste water. However, pore size distribution and surface chemistry should also be considered while selecting a good adsorbent. (Hutchins, 1997; Ahmedna, 2000a).

- ✓ **Pore size distribution**

The total porous structure of silica gel is formed by a wide range of pore sizes. For practical reasons, pore sizes are classified into three main types . This classification is arbitrary and was developed based on the adsorption of nitrogen at its normal boiling point on a wide range of porous solids International Union of Pure and Applied Chemistry (IUPAC) (Sing et al, 1985):

macropores (d> 50 nm), mesopores (2< d< 50 nm), and micropores (< 2 nm).

A silica gel with substantial mesoporisity is generally recommended for adsorption of methylene blue from waste water treatment, It is silica based nanoparticles containing many empty channels (mesopores) arranged in a honeycomb-like pore configuration and It offer unique structural properties such as large pores, tunable pore diameter, large surface area, ordered and stable mesostructure, dual functional surfaces(exterior and interior pore surfaces), and modifiable morphology (Trewyn *et al.*, 2007). The presence of high microporosity would make adsorption of larger molecules, as found in the process, problematic.These large molecules would have difficulty entering and navigating through the micropores with the possibility that the micropores could become clogged, thereby effectively closing down further adsorption (B. Pendyal (1998).

Chapter Three

Material and methods

3.1 Material

3.1.1 Raw Material preparation

The Bottom ash (BA) used for silica extraction was collected from Reppi waste to energy, colfe keraniyo, around Addis Ababa, Ethiopia. From the collected BA sample plastic and unburned materials were collected manually, then the sample was washed with distilled water for the removal of grass and other low dens materials then dried at105^0c for 12h, Then the bottom ash sample was ground by using an electrical grinder (cross beater mill) and sieve using USA test standard stainless steel sieves to obtain samples of 0.075mm. The BA was pretreated, by the solid dispersion leaching treatment method, which increases a potential silica extraction by reducing heavy metal compounds. It was done in the presence of 1N hydrochloric acid with the ratio of 1: 3 (wt: vol) between BA and hydrochloric acid, the mixture was stirred slowly for 24 h at 20^0C. After this pretreatment, the mixture was left standing for 48 h to facilitate the precipitation of impurities such as iron and calcium. Subsequently, the mixture was filtered to remove impurities and to separate the treated bottom ash (TBA). The TBA was washed sufficiently with distilled water several times until the filtrate became neutral; this result indicates the complete removal of heavy metals from bottom ash. Afterward, the sample was dried in the oven at 105 °C for 12 h before extraction and used for the next experimental work. The chemical composition result for raw material has been done for the next experimental work.

3.1.2 Chemicals

Methylene blue solution chemical formula, $C_{16}H_{18}N_3ClS$ and molecular weight of 319.5 was used for the adsorption experiments,NaOH used for the extraction of silic in the form of sodium silicate; HCl was used to promote the gel formation by acidifing sodium silicate to form hydrosol and ammonia used to condensation and to reduce aginig time hydrogel. Distilled water was used for removing sodium and chlorine ion to make sure stable and pure gel.

3.1.3 Instrument

A magnetic stirrer was used for the desired temperature with stirring. An oven was used for drying the wet ash and gel. Fourier transform infrared (FTIR) analysis was also carried out to know what bonds are present in the prepared silica gel(siloxane and silanol groups) and to identify the purity of amorphous SiO_2. Brunauer-Emmett-Teller (BET) was used to determine Surface area, pore volume and pore diameter. A UV- spectrophotometer was used to determine the absorbance. The pH meter was used to measure the pH of solution. Conical flask were used to handle the solutions. A meter balance was used to weigh the samples. Pipette has been used to transfer the solution into the test tube.

3.2 Methods

3.2.1 Synthesize of Xerogel

In this study,The preparation of silica gel from treated BA was done.Briefly, silica gel was made in two steps

- ✓ **Extraction of silica from the treated bottom ash (TBA)**

The extraction of silica from the TBA was studied by varying the reaction time (1, 2 and 3 h), NaOH concentration (1, 2 and 3 M), and solid to liquid ratio ((wt: vol): 1:1,1:2, and,1:3) to ascertain the optimal conditions for silica extraction. The extraction experiments were performed by adding 25g of TBA into different concentrations and volumes of NaOH solvent, the mixture was heated at a temperature of 75^0C with constantly slow stirring by using a magnetic stirrer to dissolve silica. Then the sample was cooled for l h and filtered by filter paper, the residue after the extraction experiments were carefully filtered and analyzed via atomic absorption spectrometer (AAS) to quantify the remaining silica. The clear colorless filtrate solution contains the sodium silicate solution (SSS), which was used to obtain silica gel. The effects of the reaction time, concentration, and solid to liquid ratio were obtained on the dissolution of silica from treated bottom ash, which was analyzed on the purity of the final product silica gel.

✓ **Synthesis of the silica xerogels**

Synthesis of the silica xerogels consists of three steps: hydrolysis, condensation, and drying. For the hydrolysis, 2.5N HCl solution was added dropwise into sodium silicate solution, until the solution becomes acidified pH 3. It was added while stirring vigorously for 19 min at room temperature in a sealed container. These processes were also incubated to promote gel formation and to increase the surface area of silica gel. For condensation, the hydrolyzed silica sol was mixed with 40 ml water before the addition of ammonia. Then ammonia (NH_4OH, 33%) was added drop-wise with no further stirring, to promote condensation, and the resulting homogeneous sol was left to gel, it also used to reduce aging time. Hydrogel formed after aging time at room temperature for 18 hours. The Hydrogel (soft gel) was collected and washing until the pH become 7 which indicates the complete removal of sodium and chlorine ions. The pores are also interconnected by water then dried at 105^oC for 24 hours to remove moisture and to produce dried silica xerogels. The Silica xerogel was then placed in a high-temperature furnace at 550^0C for 6 h for calcinations to remove surfactant the material was grinded in an agate mortar and pestle the particles having size 0.1mm (140 mesh ASTM standard) and packed in a plastic bottle for further use. Synthesis of the silica xerogels from the bottom ash experimental setup was shown in fig 3.1.

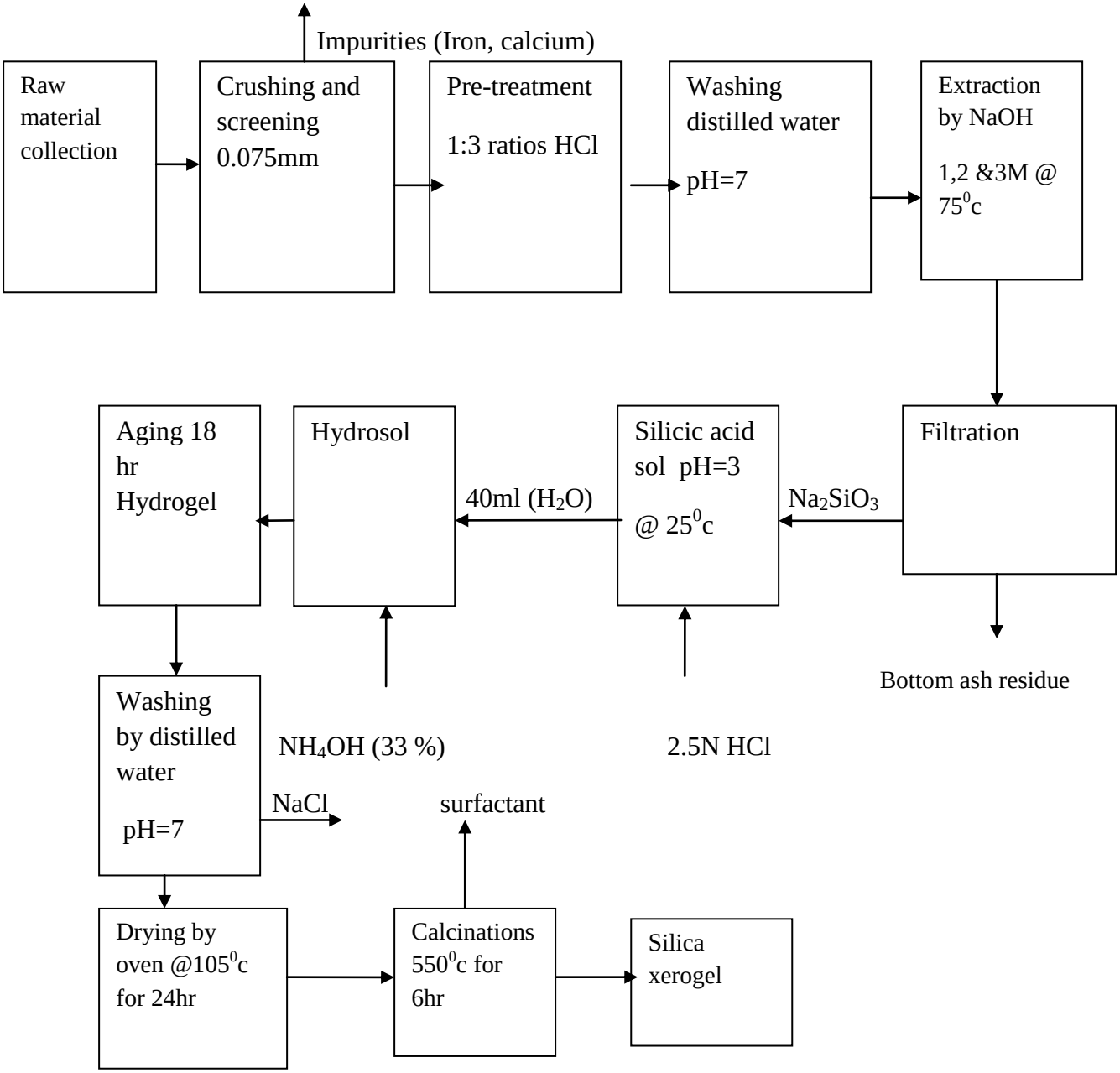

Figure 3.1 process flow diagram

3.3 Characterization of the Prepared silica xerogel

✓ **Determination of Moisture Content**

Moisture content of the extracted silica was estimated according to (Okoronkwo et al., 2013). Approximately 1 g of silica gel was heated in aluminum moisture pans at 130^0C for 1 h. Then the samples were cooled in a desiccator and weighed to record the weight loss (%) of the samples**.**

The percentage moisture content was computed as follows:

$$\text{Moistur content}\% = \frac{loose\ in\ weight\ on\ drying}{initial\ sample\ weight} * 100 \quad \text{.....3.1}$$

✓ **Determination of Bulk density**

Bulk density of the prepared silica xerogel was done by placed in a graduated cylinder, tapped several times until constant volume to its volume and the mass measured.The bulk density is calculated as the ratio of the weight to its volume and expressed in g cm-3 (ECCMF, 1986). 20g of silica xerogel is add to 50 ml graduated cylinders, tapped several times until constant volume obtained, and measuring the weight, the bulk density was calculated as the ratio of weight to volume.

$$Bulk\ density = \frac{weight\ of\ the\ dry\ sample(gm)}{volume\ of\ packed\ dry\ materia(cm^3)} \quad \text{... ... ... (3.2)}$$

✓ **Electrical conductivity**

The ability of the samples to carry an electrical charge is tested by using aconductivity meter on aqueous solution. High conductivity values indicated that an acid or water wash was not enough to reduce leach able ash to levels observed in commercial silica gel .In this investigation samples are prepared as 1g of powder that was mixed with 100 g of distilled water and stirred for a 20 minutes before the analysis. e.g. salt dissolved in water defines the conductivity of the solution and when the number of dissolved ions increases that can be measured by a conductivity meter. The conductivity measurements are carried out to check the amount of salt released from the structure during and after the washing (Farnaz Ghajeri 2019).

✓ **Determination of purity of silica**

Purity of the silica was studied using hydrogen fluoride HF test. One gram of extracted silica was mixed with 0.5 mL HF using crucible and heated in 550^0c for 15 minute furnace.The crucible was cooled in desiccator and the residue was again weighed (N.-u. Amin et al.,2016) Purity was calculated as follow;

$$\text{purity } (\%) = \frac{weight\ loss(gm)}{weight\ taken(gm)} * 100 \ldots\ldots\ldots\ldots\ldots\ldots (3.3)$$

✓ **Determination of Surface area, pore volume and pore size**

The Brunauer-Emmett-Teller (BET) surface area of the samples was determined by nitrogen adsorption at 77 K using Micrometrics ASAP 2000 automatic surface area analyzer after the samples were dried under vacuum at 100 _C for 3 h to remove moisture. The surface area was determined using the N2 adsorption data at 77 K in the relative pressure range of 0.05–0.25, and taking the cross-sectional area of the nitrogen molecule to be 0.162 nm^2. The total pore volume was based on the N2 amount adsorbed at relative pressure greater than 0.98, and taking the liquid molar volume of N2 to be 34.65 cm^3/g at 77 K.

The average pore diameter, D, calculated from the equation based on uniform cylindrical pores as given below

$$D = 4 * \frac{Pore\ volume}{BET area} \ldots\ldots\ldots\ldots\ldots\ldots (3.4)$$

✓ **Fourier transforms infrared (FTIR) analysis**

FT-IR spectroscopy was used to identify the chemical groups present in silica xerogel. The electronic structure of silica xerogel samples were examined using FT-IR 40 x (PerkinElmer) spectrometer. The measurements were carried out over the range 4000-400cm-11 to identify types of bonds present in the particles.

✓ **The silica xerogel pH measurement**

Determination of pH was performed after washing the hydrogel then by measuring the washed water and the pH of the solution was determined using a pH-meter in order to determine basic, acid or neutral nature). The Buffer solution with a PH 4.0, 7.0 &9.0 was used as a reference.

✓ **Calibration curve preparation**

The adsorption characteristics are denoted as the quality control parameters for any silica gel. Quality control Parameters are expressed in terms of methylene blue number. Batch adsorption experiments were conducted in order to determine the maximum adsorption capacity of adsorbent. To measure this, first the standard curve between absorbance and MB concentration must be prepared to obtain this, first the methyl blue solution with different concentration 5, 7.5, 10, 12.5, and 15mg/L in 1000ml Erlenmeyer flasks was prepared, and then its absorbance was, respectively, measured by UV spectrophotometer at 665nm((λmax of MB). The standard curve was drawn according to the Lambert-Beer Law, and linear regression, the equation obtained by linear fitting is y=0.0437x–0.00316, where the correlation coefficient R^2=0.99.This large number of R^2 curve is successfully obtained. Based on this equation the adsorption efficiency was calculated**.**

3.4 Adsorption of MB dye in different factors

The adsorption tests were performed for the system adsorbate (methylene blue)-adsorbent (silica gel prepared at pH 7) to define the optimal operating conditions of the main parameters related to the adsorption process. The study of adsorption tests was performed in batch adsorption experiments with varying several parameters including contact time, initial concentration MB and dose of silica gel**.** For each run, a definite amount of silica xerogel was added to 100 ml dye solution. All the adsorption experiments were carried out at constant temperature of 25^{o}C agitator at constant shaking speed of 150 rpm. (D. Ingrachen-Brahmi et al.,2020) Adsorption of MB on developed silica xerogel was conducted with 100 ml of dye solution taken into 250 ml Erlenmeyer flasks by varying different parameters such as adsorbent dosage (0.05, 0. 1 & 0. 15g/ 100ml) and contact time (15, 30 and 45minute) and concentration of methylene blue (10, 15 and 20mg/l). The pH of the dye solutions was adjusted with 0.5M HCl or 0.5M NaOH

solution .After 1hr adsorbent and adsorbate was separated and absorbance also measured by using UVspectrophotometer at 665 nm. Then after, the final concentration of MB at the equilibrium was measured from the calibration curve. The removal efficiency of the prepared silica was calculated using the given formula as follow:

$$\%\text{Removal efficency of dye} = \frac{(\text{Co} - \text{Ce})}{\text{Co}} * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.6)$$

Where, Co is the initial concentration of dyes in (mgL-1) and; C_e is the final dye concentration a in (mgL-1) after treatment is completed.

3.5 Validation of optimum parameter on real Textile waste water

Textile Waste water was collected from dye section to check the produced silica gel dye removal efficiency at optimum condition for three times. Before and after adsorption process the waste water characterize to observe the difference between (BOD, COD, TS, Turbidity, pH and methylene blue concentration).

3.5.1 Characterizing the waste water sample

The dye house wastewaters BOD, COD, TS, turbidity, pH and color were determined by using the analytical instruments so as to know the degree which the dye-house wastewater is far from the standard discharge limits.

- ✓ **Total solid (TS) determination**:

TS concentration in water is determined by gravimetric method. A waste water sample was poured in a pre-weighed Petri dish and subjected to heat in an oven at 180^0C. The residue was then cooled in the desiccators and weighed to a constant weight. TS were calculated with the formula:

$$Ts(\text{mg/L}) = \frac{(A - B) * 1000}{Volume\ of\ Sample(mL)} \ldots\ldots\ldots\ldots\ldots\ldots (3.7)$$

where A = weight of dried residue + evaporating dish (mg); B = weight of the evaporating dish

- ✓ **Determination of Total Suspended Solids (TSS)**

TSS level in the collected water samples was determined using gravimetric method. Water sample was filtered through a pre-weighed filter paper. The filter was dried in the oven at

temperature of 105^0C overnight. The filter paper was removed and allowed to cool to room temperature in desiccators and weighted to constant weight. The increase in mass of the dry filter paper was later recorded and used for calculating TSS.TSS is calculated using the formula:

$$Tss(\text{mg/L}) = \frac{(A-B)*1000}{Volume\ of\ Sample(mL)} \dots\dots\dots\dots\dots\dots (3.8)$$

Where A = weight of the filter after filtration (mg); B = weight of the filter before filtration (mg)

- ✓ **Biological Oxygen Demand (BOD) and Chemical Oxygen Demand determination**
  BOD and COD levels in the collected water sample were determined using APHA method. Biological Oxygen Demand (BOD) is measurement of oxygen consumed in 5 day test period. BOD was measured via the winkiler method with azide modification. COD was analyzed closed reflux colorimetric method using COD digester.
- ✓ **Turbidity determination**: The turbid meter was calibrated using the standards.Then the sample was before and after adsorption was measured.
- ✓ **pH analysis:** the PH of textile waste water was determined by simply reading of pH meter which is standardized with buffer solutions of pH 4, 7 & 9.
- ✓ **MB concentration determination**: the unknown concentration of methylene blue (MB) after dying process was determind by using the above calibration curve . the waste water samples before and after adsorption the absorbance was measured by UV-spectrophotometer to see the concentration difference.the removal efficiency also calculated as follows.

  $MB\ adsorption(removal\ efficeincy)\% = \frac{(Co-C1)*100}{Co}$.....(3.9)

  Where :Co=initial concentration of methylene blue;$C_{1=}$ Final concentraton

3.6 Experimental Design

In this study, Process optimization of the experimental conditions were carried out following a standard Design-Expert 7.0.0 software Box-Behnken design (BBD) of response surface methodology (RSM). This design of the experiment helps us to optimize and set combination of process parameters with a minimum number of experiments, as well as to analyze the interaction effect between those parameters. RSM designs allow us to estimate interaction; even the quadratic effects and gives us an idea of the shape of the response surface. A Box-Behnken design (BBD) was used in the optimization of process variables with three factors at three

levels with 17 runs, including 5 central points to evaluate the effects of three independent variables such as NaOH concentration, extraction time & solid to liquid ratio on the purity of silica xerogel and also (silica gel dose, contact time & concentration of methylene blue) on methylene blue removal efficiency. The responses function was partitioned into linear, quadratic, and interactive components. The model adequacies were checked in terms of the values of R^2 and adjusted R^2. Analysis of variance (ANOVA) was employed to determine the significance of the models. Verification of optimized conditions and predicted values were done in duplicate to confirm the validity of the models.

Table 3.1: Experimental factors and levels for purity of silica xerogel

Variables	units	levels		
		-1	0	1
NaOH concentration	M	1	2	3
Solid to liquid ratio	-	1	2	3
Extraction time	hr	1	2	3

Table 3.2: Experimental factors and levels for MB adsorption

Variables	units	levels		
		-1	0	1
Contact time	min	15	30	45
Silca gel dosage	g	0.05	0.1	0.15
MB concentration	Mg/L	10	15	20

According to BBD the total number of experiment can be calculated as:

$N=K_2+K+C_P$

Where k is a number of factors, and Cp is a central replication point.

Based on this formula a Box-Behnken design (BBD) was used in the optimization of process variables with three factors at three levels with 17 runs, including 5 central points to evaluate the effects of three independent variables.

Chapter Four

Result and discussion

4.1. Raw material characterization

The chemical composition of as-received BA was disclosed by $LiBO_2$ fusion,HF attack,gravimetric,colorimetric and atomic absorption spectrometer (AAS) methods used to determine major and minor oxides, which establishes that the major components in oxide form are SiO_2 (48.88%), Al_2O_3 (14.50%), CaO (15.2%),and Fe_2O_3(8.6%).Table 4.1summarizes the chemical composition in oxide form before and after pretreatment. Due to the presence of contaminants, an acid pretreatment of BA was performed to extract heavy metals and to increase SSA(specific surface area) of the ash particles to assist the dissolution of silica afterwards. As reported in an earlier study about BA, carbonates act as a reservoir of divalent metallic ions, especially Zn, and Cu (Piantone et al., 2004). Therefore, a reduction in the content of these metals in the BA was achieved. Additionally, from the silicates group, melilite was completely dissolved along with a partial dissolution of albite and diopside. Subsequently, melilite dissolved during the pretreatment was recovered by allowing the mixture to stand unstirred. The silicates dissolved in this step were reduced and transformed into silica with a gel like structure due to the polymerization in an acidic environment (Terry, 1983). The silica in gel form was separated along with the ash residues via filtration. As a result, minimal loss of silica (1.4 wt %) during the acid pretreatment was observed and the treated bottom ash (TBA) contained 47.4 wt % of SiO_2.

Table 4.1 Chemical composition of original BA and acid treated BA (TBA) in wt. %. LOI: loss onignition, LOD: loss on dissolution after acid pretreatment.

	SiO_2	CaO	Al_2O_3	Fe_2O_3	Na_2O	MgO	K_2O	MnO	H_2O	TiO_2	P_20_5	LOI	LOD
BA	48.8	15.2	14.5	8.6	3.12	2.18	1.86	0.26	1.08	0.46	2.39	2.94	-
TBA	47.4	10.5	11.04	7.02	2.02	1.1	1.2	0.1	1	0.4	2	2.96	13.26

From the above analysis result the loss on ignition (LOI) was increased after treating, it means that there is moisture content present in the ash and there is side reaction take place by heating. If

the loss on ignition (LOI) is recorded as zero, it means that no moisture content present in the ash and no side reaction take place by heating (N.-u. Amin et al. 2016).The loss of dissolution also increase after treatment, this increase confirms the dissolution of crystalline melilite during the acid pretreatment and its precipitation as an amorphous phase. Additionally, the dissolution of other crystalline phases (calcite & dolomite) can also contribute to the increase in the amorphous content. This increase in amorphous silica is expected to enhance the dissolution of silica from the ash residues obtained after acid treatment.

Table 4.2:physical property of bottom ash

Bulk density(g/cm3)	**Electrical conductivity ms/m**	**pH**	**Moisture content (%)**
1.42	62.4	8.5	30.7

The above table shows physical property of bottom ash, the pH of the bottom ash lower than pH 9, high pH values for the tested ashes (pH > 9) may indicate high immobilization of heavy metals in the material (Monika Czop and Beata Ła´zniewska-Piekarczyk, 2019).This is confirmed by the low concentrations of the studied metals in water extracts (Table 4.2). The analyzed ashes can be an environmental problem due to their high salt content, mainly in this case. Electrical conductivity shows the availability of ions specially sodium, chlorine, iron and potassium (Monika Czop and Beata Ła´zniewska-Piekarczyk, 2019).Availability of moisture content in bottom ash also increases loss on ignition. Therefore there is side reaction.

4.2 Experimental Design and Statistical Data Analysis of silica xerogel

Results for silica xerogel production by using bottom ash as a precursor with different parameters such as time, solid to liquid ratio and chemical concentrations were evaluated on the effect of purity of silica gel. There were about 17 numbers of experimental run as per by a standard Design-Expert 7.0.0 software Box-Behnken design (BBD) of response surface methodology (RSM).

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standard Design-Expert 7.0.0 software Box-Behnken design (BBD) of response surface methodology (RSM).

Table 4.3: Statistical analysis of silica xerogel purity

Run NO	**Factor 1**	**Factor 2**	**Factor 2**	**Respons**
	A:NaOH concentration M	**B:ratio S(1)/L**	**C:Extraction Time hr**	**Purity (%)**
1	2.00	2.00	2.00	85.29
2	1.00	1.00	2.00	62.427
3	3.00	1.00	2.00	64.951
4	1.00	2.00	1.00	62.579
5	1.00	3.00	2.00	65.936
6	2.00	3.00	1.00	66.495
7	3.00	2.00	3.00	81.901
8	3.00	2.00	1.00	64.95
9	3.00	3.00	2.00	73.25
10	2.00	2.00	2.00	85.44
11	2.00	1.00	3.00	76.862
12	1.00	2.00	3.00	75.386
13	2.00	2.00	2.00	85.75
14	2.00	1.00	1.00	65.49
15	2.00	2.00	2.00	85.59
16	2.00	2.00	2.00	85.751
17	2.00	3.00	3.00	85.753

From the analysis of the above table, it is observed that the maximum and minimum is 62.427 and 85.751 % respectively purity of silica gel. Based on these results of the different parameters the relationship and the interaction of the combination of these parameters on the percent(%) of purity have been studied graphically.

4.2.1 Analysis of Variance for the Data (ANOVA)

Based on the analysis of variance (ANOVA) as shown in Table 4.4,the models which correlate the study parameters with the responses (purity) were found significant with F-value of 1399.69 and ($p<0.0001$). Values of "Prob > F" less than 0.0500 indicate model terms are significant.In this case A, B, C, AB, AC,BC, A^2, B^2, C^2 are significant model terms.Values greater than 0.1000 indicate the model terms are not significant.If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The lack of fit test measures the failure of the model to represent the data in the experimental domain at points which are not included in the regression (Miafo APT et al.,2015) As shownin Table 4.4,the F and p values of lack of fit test werefound 5.52 and 6.62% for purity of silica gel which imply that the“lack of fit”was not significant and indicates that the model equations are adequate for predicting the purity. There were 6.62% chances that“lack of fit F-values”such large could occur due to noise for the two experimental responses, respectively.

Table 4.4: Design expert output (ANOVA) for preparation of silica xerogel purity

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	1486.47	9	165.16	1399.69	< 0.0001	significant
A-NaOH concen.	*43.82*	*1*	*43.82*	*371.39*	*< 0.0001*	
B-ratio	*58.88*	*1*	*58.88*	*499.01*	*< 0.0001*	
C- time	*455.84*	*1*	*455.84*	*3863.06*	*< 0.0001*	
AB	*5.74*	*1*	*5.74*	*48.61*	*0.0002*	
AC	*4.29*	*1*	*4.29*	*36.38*	*0.0005*	
BC	*15.55*	*1*	*15.55*	*131.76*	*< 0.0001*	
A^2	*480.68*	*1*	*480.68*	*4073.55*	*< 0.0001*	
B^2	*285.79*	*1*	*285.79*	*2421.94*	*< 0.0001*	
C^2	*56.88*	*1*	*56.88*	*482.07*	*< 0.0001*	
Residual	0.83	7	0.12			
Lack of Fit	*0.67*	*3*	*0.22*	*5.52*	*0.0662*	*not significant*
Pure Error	*0.16*	*4*	*0.040*			
Cor Total	1487.29	16				

4.2.2 Model fit summary

The sequential model fittings presented in Table 4.5 indicate that quadratic model was suggested for this experimental responses by design expert. From the lack of fit tests, it is clear that the second-order quadratic model was suitable (prob >F is 0.0001). Insignificant lack of fit is desirable for a model to fit the given experimental data property.

Table 4.5 Sequential model fitting for purity

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	95445.23	1	95445.23			
Linear vs Mean	558.55	3	186.18	2.61	0.0962	
2FI vs Linear	25.58	3	8.53	0.094	0.9614	
Quadratic vs 2FI	902.35	3	300.78	2549.01	< 0.0001	Suggested
Cubic vs Quadratic	0.67	3	0.22	5.52	0.0662	Aliased
Residual	0.16	4	0.040			
Total	96932.53	17	5701.91			

The coefficient of determination (R^2), shown in Table 4.6, for the regression model of purity was 0.9994, which implies that the models accounted for 99.94% variability within the experimental range.Furthermore, the"predR^2"values of 0.9927 in reasonable agreement with the"AdjR^2"of 0.9987. The model equations can also predict the responses (purity) with predR^2 of 99.27% variability while the study factors are out of the experimental range. In general, for a good model,the values of R^2 and prediction R^2 should be close to 1.The"adeq Precision"measures the signal to noise ratio and it is always desired to be greater than 4 and the values obtained (89.319) show that noise is very low. In conclusion, the suggested quadratic model can be used to navigate the design space with good accuracy.

Table 4.6Model summary statistical for purity

Std.Dev	0.34	R-Squared	0.9994
Mean	74.93	Adj R-Squared	0.9987
C.v.%	0.46	Pred R-Squared	0.9927
Press	10.90	Adeq precision	89.319

4.2.4 Regression Model Equation

Design-expert was applied to analyze results on the purity of silica xerogel and a first order regression equation, with the interaction terms, of the form, the final model equation in terms of actual factor was presented by equations representing the variation of purity of silica xerogel with independent factors.

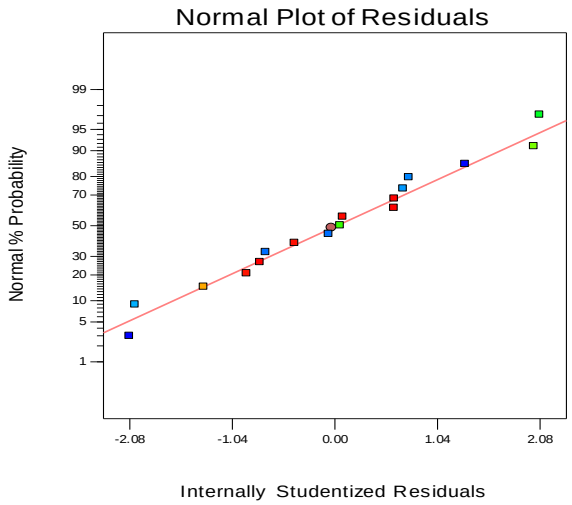
Final Equation in Terms of actual Factors:

Puriy=-13.21500+40.61190*A.+29.32940*B+16.23590*C+1.19750 * A.* B +1.03600 * A* C+1.97150* B * C-10.68460*$A.^2$-8.23860*$B^2$3.67560*C^2……..…….(4.1)

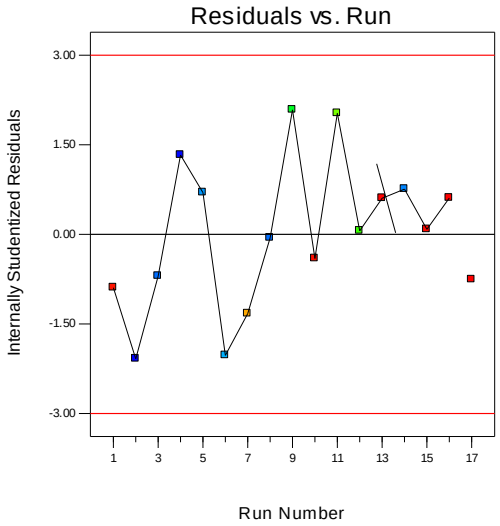
Where A: NaOH concentration ,B: ratio of Solid to Liquid(S/L) and C:Extraction time

4.2.5 Diagnostic Test for the Response

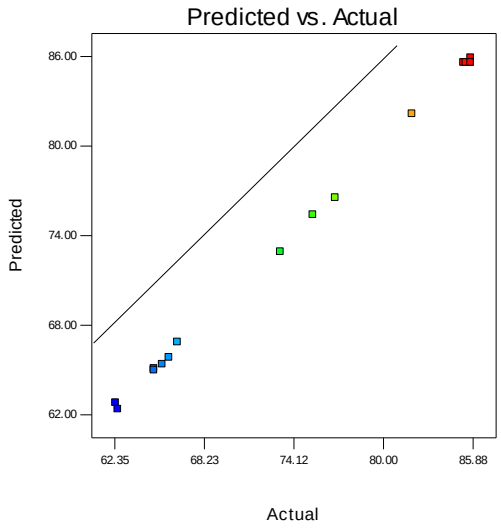
Diagnosing of the statistical properties of the model after post ANOVA analysis is the necessary part before going for examining the model graphs and optimization. Normal probability plot of studentized residual for the diagnosing for model adequacy checking, the data points should be approximately linear and a nonlinear pattern (look for an S-shaped curve) indicates non-normality in the error term. The normal probability plot, indicates the residuals following a normal distribution, in which case the points follow a straight line(Fig 4.1a).This indicates the model satisfies the assumption of ANOVA. Internally studentized residuals plot which were constructed to visualize the satisfactory fit of the developed model and the plots (Fig. 4.1b) show that all the data points lie within the limits (±3). The predicted values obtained from the developed model were quite close to the experimental values and lie reasonably close to the straight line and indicate the adequate agreement with real data (Fig.4.1c). The results suggest that the models can be used to predict the optimum condition for the production of pure silica gel.



(a)



(b)



(c)

Fig 4.1: Diagnostic plot for purity of silica gel

4.2.6 The interaction effect of process variables on the purity

- ✓ **Interaction of NaOH conentration and ratio of solid to liquid on purity of silica**

From fig 4.2, solid/ liquid ratio to NaOH concentration had an interaction effect and the variation of one factor has a significant influence on the other factor. As a result, the target response was significantly affected by the interaction of NaOH concentration and ratio of solid to liquid. The 3D response surface plot shows at the beginning; minimum NaOH concentration with a minimum solid liquid ratio to get less purity silica gel was obtained because, In an alkaline media silicate dissolution depends on the transfer of soluble silica species away from the extracted particles (Strachan, 2001).Therefore the low concentration of sodium hydroxide was not completely extract silica rather than other ions from bottom ash. However, at the center of the 3-D graph shows when the concentration and the ratio increased, the highest purity of silica gel was obtained because, concentration and volume of sodium hydroxide increase, the silica extraction capacity is more than others ions and also the volume increasing also help to facilitate fast silica extraction. At the end of the 3-D graph shows both increase NaOH concentration and ratio, the purity of silica gel decrease because, both factors increasing will increasing the extracted amount of trace elements from bottom ash and in addition the loss of ignition /side reaction increased during the extraction of sodium silicate this is also reduce purity. It is concluded that concentration of NaOH can play significant role in favor of purity of silica gel previously reported (Strachan, 2001). In fact, about 85.573 of purity value was found at 2M of concentration NaOH with the ratio of 1:2 solid to liquid ratio a major role in the purity of silica gel.

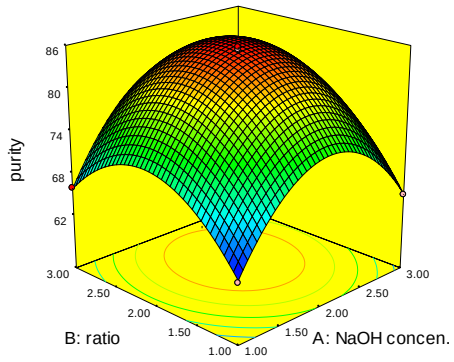


Figure 4.2 Interaction of ratio and NaOH

✓ **Interaction of NaOH conentration and extraction time on purity of silica**

Fig 4.3 shows the interaction between NaOH concentration and extraction time on purity of silica gel. The result shows the interaction of NaOH concentration with extraction time the optimum result obtained at the center of surface because further increasing of both factors will increase the extracted amount of trace elements from bottom ash and in addition the loss of ignition /side reaction increased during the extraction of sodium silicate this is also reduce purity. It is concluded that concentration of NaOH and time can play significant role in favor of purity of silica gel previously reported (Strachan, 2001).

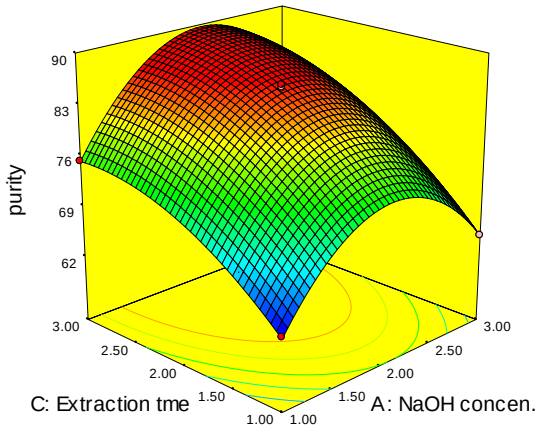


Figure 4.3 interaction effect of extraction time and NaOH

✓ **Interaction effect of ratio and extraction time on purity of silica**

As the interaction graph of extraction time and ratio indicated below in figure 4.5 the purity of silica gel is high at the center. both factors increasing effect will increase the extracted amount of trace elements from bottom ash and inaddition the loss of ignition /side reaction increased during the extraction of sodium silicate this is also reduce purity.

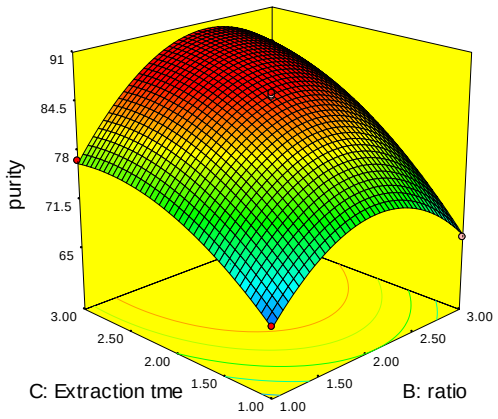


Figure 4.4 interaction of ratio and NaOH

4.2.7 Optimazation of Process Variables

Within the scope this research,Optimization of process parameters which lead to an silica xerogel with a good characteristic was carried out after observing all the effects of variables. It is to note that results obtained when studying the effect of individual parameters (extraction time, solid/liquid ratio and NaOH concentration) on the purity of silica gel. Table 4.6 shows that, the optimum working conditions (ultimate goals, high and low limits) of the response and factors (extraction time, solid/liquid ratio and NaOH concentration) employed during the optimization analysis.

In view of the optimization, the targeted criterion was increase purity while the factors values were set in the range studied.

Table 4.7: Optimization constraints and solutions for purity of silica xerogel

Name	Goal	Lower Limit	Upper Limit
NaOH concentration	Target =2	1	3
Solid /liquid ration	Minimize	1	3
Extraction time	In range	1	3
purity	Maximaz	62.427	85.751

Solutions

Number	NaOH concen.	ratio	Extraction tme	purity	Desirability	
1	2.00	1.50	2.50	84.1321	0.901	Selected
2	2.00	1.51	2.57	84.0743	0.901	
3	2.00	1.50	2.51	83.5494	0.900	

Based on the optimization result bottom ash at 2.50 h extracted time, 2M NaOH concentration and solid/liquid ratio (1.5) can give the best silica xerogel with high purity (84.1321). To validate the optimum condition predicted by the model,triplicate experiments were conducted at the optimized carbonization processconditions.Accordingly,purity valu84.1311ofwere obtained.This result is in close agreement with the predicted data obtained from the optimization analysis. he small percentages of error of 0.01% between the optimization and the validation results, further confirm that the models are suitable and sufficient to predict the responses.

4.3 Characterization results of silica xerogel

After obtaining the best silica xerogel with better methyl blue adsorption,the selected silica xerogel characterization which are FTIR,BET, purity,bulk density, moisture content pHvalue and electrical conductivity were done and the results discussed as follow.

Table 4.8 physical and chemical property of silicagel

Moisture content(%)	**Bulk density**	**pH**	**Electrical conductivity**	**Purity(%)**	**Volumof sodium silicate (ml)**	**Wt. of silica gel (gm)**
5.26%	0.73g/cm^3	7	0.27µS/cm	84.132%	20	2.1

The above table shows that the moisture content and bulk density of this sample is close to commercially available silica gels but the commercially available silica gel purity between 94-96%. It is clear from the table that silica extracted is 84.1321% purity which is the maximum possible purity of the extracted amorphous silica gel in this study. From the result the remaining 5% constitutes moisture and other elements like alumina, sodium, calcium etc (Noor-ul Amin et al., 2016). The presence of moisture in the silica may be due to the incomplete drying the silica after precipitation and trace amount of elements may be due to insufficient acid washing of bottom ash before silica extraction the electrical conductivity result also shows there is some ions dissolve in the distilled water such as Na^+ and Cl^- ions. The pH value indicates the complete removal of salt (NaCl).

The purity of the sample was reduced; to identify this reason the residue (bottom ash) after extraction (EBA) was analyzed via $LiBO_2$ fusion,HF attack,gravimetric,colorimetric and atomic absorption spectrometer (AAS) methods used to quantify the remaining silica and the dissolution of other chemical amount with the extracted silicate solution.

Table 4.9 Chemical composition of BA after extraction , LOI: loss on ignition and LOD: loss on dissolution

	SiO_2	**CaO**	**Al_2O_3**	**Fe_2O_3**	**Na_2O**	**MgO**	**K_2O**	**MnO**	**TiO_2**	**P_2O_5**	**H_2O**	**LOI**	**LOD**
BA after Extraction	0.17	9.85	10.3	6.8	2.01	1	1	0.01	0.2	1.9	0.9	3.06	62.75

This result shows almost all of Silica oxide extracted from bottom ash but, other oxides also extracted with silica from the bottom ash this is also shows that the purity of the silica xerogel

were decreased. From the table 4.1 and 4.9 the result compared between treated bottom ash and extracted bottom ash compositions, that the result shows how the purity reduce during extraction of silica, 0.65 of CaO, 0.74 of Al_2O_3, 0.22 of Fe_2O_3, 0.01 of Na_2O, 0.2 of K_2O, 0.2 of TiO_2 and other oxides extracted with SiO_2 this also reduced the purity of silica gel. The loss on ignition also was increase after extraction of silica this means there is moisture content present in the ash and there is side reaction take place by heating. The loss on dissolution also highly increased it means the amorphous silica content increase because the other crystal silica also dissolves in the form of amorphous silica, therefore amount of silica increase during the extraction.

4.3.1Fourier transforms infrared spectroscopy analysis (FTIR)

A Fourier transform infrared (FTIR) spectra of the extracted silica is shown in Fig.4.5. The spectra show the major chemical groups present in the prepared silica gel.The broad band at 3256 cm^{-1} is due to the stretching vibration of the OH bond from the silanol group (Si-OH) resulting from the absorbed water molecules on the silica surface (Venkatathri, 2007; Zawrah et al., 2009).The band at 1060-1100 $cm^{-1}$is due to asymmetric stretching vibration of the siloxane bonds (Si-O-Si) (Velmurugan et al., 2015; Amin, 2014),while the band at 791-806 cm^{-1} is assigned to Si-O-Si symmetric bond stretching vibration.The band at 620 cm^{-1} is associated with network O-Si-O bending vibration modes (Amin et al., 2016).

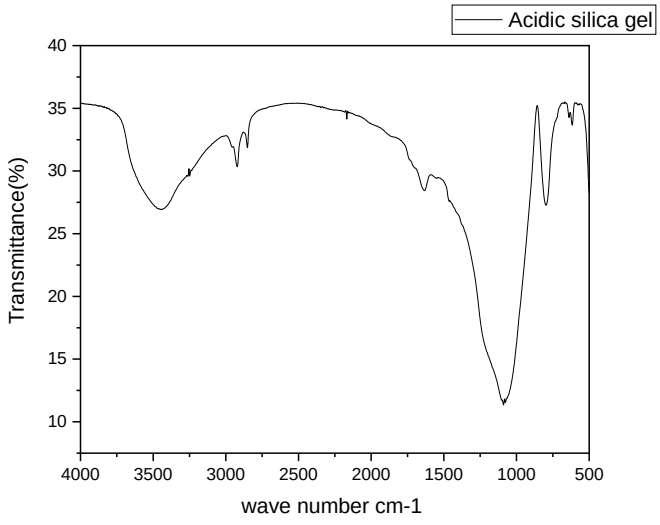


Figure 4.5 FTIR spectrum of silica gel

4.3.3 Brunauer-Emmett-Teller (BET) analysis of silica xerogel

The observations in BET were further confirmed by the pore size and the pore volume of the silica gel (Table 4.10). The material prepared presents a pore volume of 10.4cm3/g, with a pore diameter of 18.38Å. These results confirm the mesoporous character of the synthesized silica gels (pore diameter under of 50Å).

Table 4.10 Surface area, pore volume and average pore radius of silica gel sample prepared from by-bottom ash

BET surface area (m^2/g)	**HK method**		
253.1	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore radius(A°)
	184.4	10.4	18.38

The BET result shows the surface area of silica gel 253.1 m^2/g at the pH 3 hydrosol,since from the litratare rivew the pure silica gel which prepared from sodium silicate and sulfuric acid, the surface area of silica gel is 632 m^2/g which results indicate the purity of silica affected by source of silica obtained materials this is also affect the surface area of the adsorbents. A typical good quality adsorbent silica gel has residual water contents of about 6 %, is hydrophilic, and has a surface area of 200-800 m^2 /g (Kirk Othmer, 1997).Therfore surface area of produced silica gel results confirm the good quality adsorbent character **.**

4.4 Adsorption of MB by the optimum product silica xerogel

4.4.1 Statistical Analysis on adsorpition efficiency

Optimization of the removal efficiency parameters was done using the chosen silica xerogel Optimization was carried out using BBD design with three factors (silica xerogel dosage, contact time and MB concentration) and one response (% removal efficiency/MB adsorption). Statistical analysis was carried out to determine correlation coefficients of the model as a function of the responses.

Table 4.11expermental runs for MB adsorption

	Factor 1	Factor 2	Factor 3	Response
Run no	**A:Contact time**	**B:MB concentration**	**C:Silica dosage**	**Methylen blue adsorption**
	minu	**Mg/L**	**g**	**(%)**
1	15.00	15.00	0.05	30.58
2	15.00	15.00	0.15	73.525
3	30.00	15.00	0.10	85.492
4	15.00	10.00	0.10	61.901
5	15.00	20.00	0.10	63.95
6	45.00	10.00	0.10	85.53
7	30.00	10.00	0.15	85.516
8	45.00	20.00	0.10	65.25
9	30.00	15.00	0.10	85.101
10	30.00	15.00	0.10	85.19
11	30.00	15.00	0.10	84.278
12	45.00	15.00	0.15	85.531
13	30.00	10.00	0.05	43.985
14	30.00	20.00	0.05	30.69
15	30.00	20.00	0.15	82.36
16	45.00	15.00	0.05	38.862
17	30.00	15.00	0.10	85.466

From the analysis of the above table, it is observed that the maximum and minimum 30.58 is and and 85.531% MB adsorption. Based on these results of the different parameters the relationship and the interaction of the combination of these parameters on percent(%) of color removal have been studied graphically.

4.4.2 Analysis of variance

Based on the analysis of variance (ANOVA) as shown inTable 12,the model which correlate the study parameters with the responses (MB removal efficiency) was found significant withF-value of 946.22 and ($p<0.0001$).In the two tables, the values of"Prob>F"less than 0.05 indicate model terms are significant, whereas values greater than 0.1000 indicate the model terms are not significant. Accordingly, for MB adsorption, the model terms terms A,B,C, AB, BC, A^2, B^2, and C^2 were found significant.

The F and p values of lack of fit test were found 6.43 and 0.0521 for MB adsorption which imply that the"lack of fit"was not significant and indicates that the model equations are adequate for

predicting the MB adsorption.There was 5.21% chances that"lack of fit F-values"such large could occur due to noise for the experimental response..Significant lack of fit is bad -- we want the model to fit. This relatively low probabiity (<10%) is troubling.

Table 4.12: Analyses of Variance for response surface quadratic model for methylene blue removal efficiency

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	6877.96	9	764.22	946.22	< 0.0001	significant
A-contact time	*255.47*	*1*	*255.47*	*316.31*	*< 0.0001*	
B-MB CONC.	*150.28*	*1*	*150.28*	*186.07*	*< 0.0001*	
C-Silica dosage	*4177.67*	*1*	*4177.67*	*5172.61*	*< 0.0001*	
AB	*124.55*	*1*	*124.55*	*154.21*	*< 0.0001*	
AC	*3.47*	*1*	*3.47*	*4.29*	*0.0770*	
BC	*25.70*	*1*	*25.70*	*31.82*	*0.0008*	
$A^2 3$	*98.75*	*1*	*398.75*	*493.72*	*< 0.0001*	
B^2	*162.81*	*1*	*162.81*	*201.59*	*< 0.0001*	
C^2	*1402.26*	*1*	*1402.26*	*1736.22*	*< 0.0001*	
Residual	5.65	7	0.81			
Lack of Fit	*4.68*	*3*	*1.56*	*6.43*	*0.0521*	*not significant*
Pure Error	*0.97*	*4*	*0.24*			
Cor Total	6883.61	16				

4.4.3Model fit summary

The sequential model fittings presented in Table 4.13 indicate that quadratic model was suggested for the experimental response by design expert. From the lack of fit test, it is clear that the second-order quadratic model was suitable (prob > Fis 0.0001). Insignificant lack of fitis desirable for a model to fit the given experimental data properly

Table 4.13: Sequential Model Sum of Squares for methylene blue removal efficiency

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Mean vs Total	80964.33	1	80964.33			
Linear vs Mean	4583.41	3	1527.80	8.63	0.0021	
2FI vs Linear	153.71	3	51.24	0.24	0.8674	
Quadratic vs 2FI	2140.83	3	713.61	883.56	< 0.0001	Suggested
Cubic vs Quadratic	4.68	3	1.56	6.43	0.0521	Aliased
Residual	0.97	4	0.24			
Total	87847.94	17	5167.53			

The coefficient of determination (R^2), shown in Table 4.14, for the regression model of MB adsorption 0.9992, which implies that the models accounted for 99.92% variability within the experimental range.Furthermore, the"predR^2"values of 0.9889 in reasonable agreement with the"AdjR^2"of 0.9981. The model equations can also predict the responses (MB adsorption) with predR^2 of 98.89% variability while the study factors are out of the experimental range. In general, for a good model,the values of R^2 and prediction R^2 should be close to 1.The"adeq Precision"measures the signal to noise ratio and it is always desired to be greater than 4 and the values obtained (82.705) show that noise is very low. In conclusion, the suggested quadratic model can be used to navigate the design space with good accuracy.

Table 4.14 Model summarystatistical for MB adsorption

Std. Dev.	0.90	R-Squared	0.9992
Mean	69.01	Adj R-Squared	0.9981
C.V. %	1.3	Pred RSquared	0.9889
PRESS	76.43	Adeq Precision	82.705

The "Pred R-Squared" of 0.9889is in reasoable agreement with the "Adj R-Squared" of 0.9981. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable.Your ratio of 82.705 indicates an adequate signal. This model can be used to navigate the design space.

4.4.4 Development of regression model equation

The equations generated from the fitted surface response 2FI and quadratic models for the removal efficiency of methylene blue is shown in Equations (4.3). Kumar et al. (2008) stated that when regression coefficient has a positive sign, the increase of the associated factor causes an increase in response and a negative sign would cause a decrease in the optimization parameter.

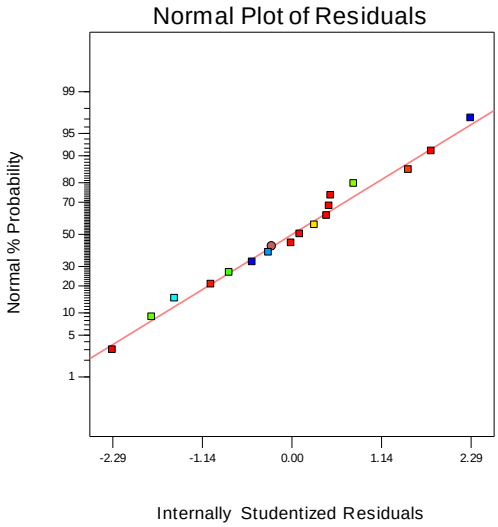
Final Equation in Terms of Actual Factors:

MB removal efficiency = -141.33400+3.96369* A+7.81326* B.+1727.65850*C-0.074400* A*B.+1.24133*A*C+10.13900*B*C-0.043251*A^2-0.24873*$B^2$7299.73000*C^2……(4.3)

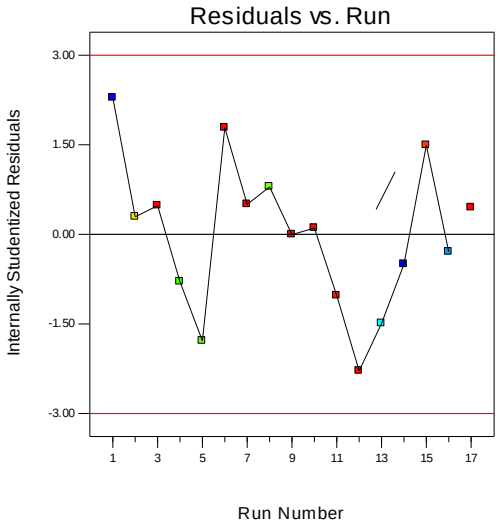
Where A: Contact time Concentration of MB and C: Silica gel dosage.

4.4.5 Diagnostic plots

The adequacy of the models was further checked by constructing different diagnostic plots in order to find out whether the model equations would give sufficient approximations to the actual values. Fig 4.6a show that the normal % probability plot of residual for the responses is normally distributed, as the data lie reasonably close to the straight line and show no deviation of the variance.Internally studentized residuals plot which were constructed to visualize the satisfactory fit of the developed model and the plots (Fig. 4.6b) show that all the data points lie within the limits (±3). The predicted values obtained from the developed model were quite close to the experimental values and lie reasonably close to the straight line and indicate the adequate agreement with real data (Fig.4.6c). The results suggest that the model can be used to predict the optimum condition for the removal of MB.



(a)



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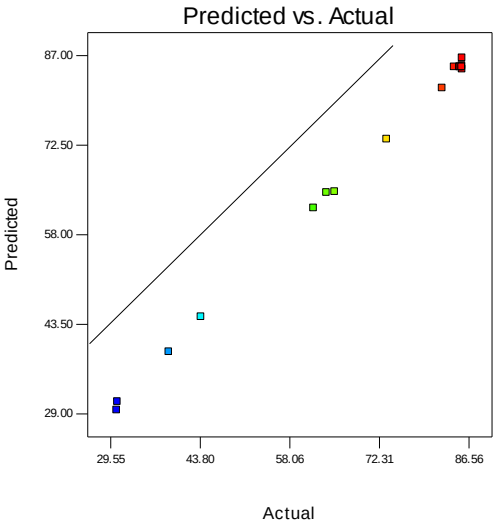

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Figure 4.6 a,b and c diagnostic plot

4.4.6 The interaction effect of process parameters on removal efficiency

✓ **The interaction effect of MB concentration and contact time**

Fig 4.7 result shows the effect of MB concentration to contact time on effect of adsorption efficiency. The 3D response indicates that the removal efficiency decrease with increasing concentration, the fast adsorption process at minimum concentration of dye of the reaction has the large number of active sites available and also increases with time but after 30min it becomes slow. The fast adsorption process at the beginning of the reaction can be explained by the large number of active sites available, and gradually as the recovery rate of the surface increases, the accessibility of the remaining vacant sites becomes difficult, as a result, the rate of adsorption becomes slow (Y. L. Ma et al., 2004).

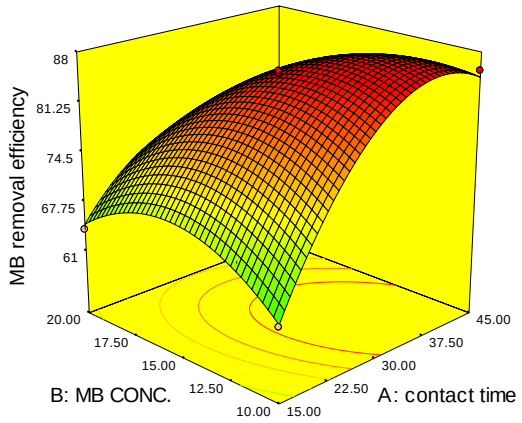

Figure 4.7 Interaction effect of MB concentration and contact time

✓ **The interaction effect of silica dosage and MB concentration**

Fig 4.8 shows significant interaction between MB concentrations and silica dosage on the methylene blue adsorption/removal efficiency of silica gel. The result indicates that the uptake of the dye increases with the dosage of the silica gel and that the maximum dye removal was achieved for a minimum concentration of dye, in this presence of a high number of active sites in this mass interval of silica gel. Beyond 0.1mg/l the dosage, the results clearly indicate that the removal efficiency increases to an optimum value from which further increase in the adsorbent

dosage has no significant effect on them. Thus restricts the active surface area available for dye adsorption (D. Ingrachen-Brahmi et al., 2020).

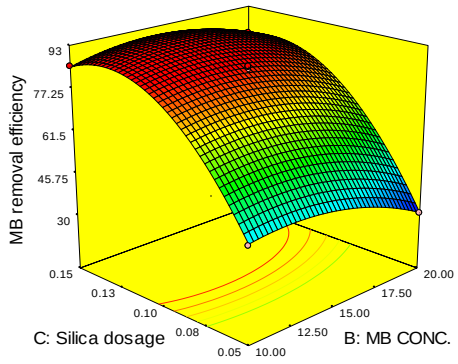

Figure 4.8 The interaction effect of silica dosage and MB concentration

- ✓ **The interaction effect of silica dosage and contact time**

As shown in the fig 4.9, the MB adsorbing efficiency of silica gel is positively affected by time as well as by silica dosage. As increase time and silica gel, the percentage of MB removal efficiency become increase. This can be explained by the presence of a high number of active sites in this mass interval. While after reaches at equilibrium further increasing both time and silica dosage can lead to an insignificant change in removal efficiency.

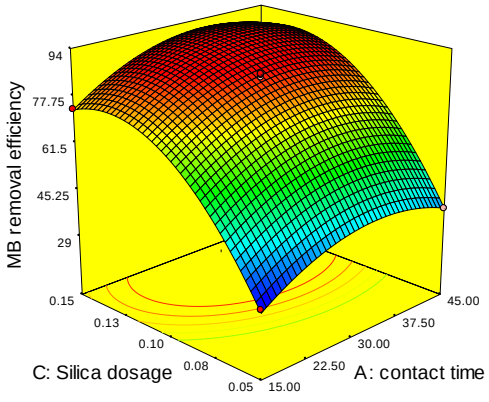

Figure 4.9 The interaction effect of silica dosage and contact time

4.4.7 Finding the optimal dye removal process parameters for MB adsorption

Optimization was carried out after observing all the effects of color removal. The objective is to maximize removal efficiency. Three solutions were found and the solution with the highest desirability was chosen. In other to verify the optimization results, the selected parameters were validated by textile waste water in the laboratory with suggested values as shown in Table 4.15. The result from the experiments confirmed the selected solutions.

Table 4.15 Optimization constraints for removal efficiency of dye

Name	Goal	Lower Limit	Upper Limit
Contact time	minimize	15	45
MB Conc.	Is in range	10	20
Silica dosage	is target = 0.10	0.05	0.15
MB removal	maximize	30.58	85.531

solutions

Number	Contact time	MB Conc.	Silica dosage	MB removal	Desirability	
1	30.85	13.94	0.10	86.101	0.99	Selected
2	33.35	10.06	0.10	86.114	0.99	
3	41.84	14.86	0.10	86.076	0.96	

To validate the optimum predicted condition by the model, triplicate experiments were conducted on textile dye house waste water with optimum product silica xerogel.

4.5 Adsorption on textile waste water

Textile wates water from dye section were collected from company and the following waste water characterization before and after adsorption were done in the laboratory.

Table 4.16 Textile waste water characterization before and after adsorption

Property of textile waste water	**pH**	**Concentration Methylene blue(mg/L)**	**BOD (mg/L)**	**COD (mg/L)**	**Turbidity (NTU)**	**TSS(mg/L)**	**TS (mg/L)**	**MB Removal Efficiency (%)**
Sample collected	8.2	14.81465	163	506.8	162	0.17	0.2	
Run 1	8	2.278	162.5	456.12	161.81	0.15	0.18	84.62
Run 2	8	2.279	162.4	455.8	161.79	0.15	0.18	84.61
Run 3	8	2.278	162.5	455.2	161.79	0.15	0.18	84.62

From the result of Table 4.16 shows that the dye house wastewaters are highly colored which can be hazardous to the environment if it is disposed untreated. The COD values are also much higher and other values also very far from the free discharge limit shown in Table 2.2. Though the BOD values are relatively low as compared to other wastewater types, they are still above the free discharge limit.

Turbidity and color of the wastewater are extremely higher than the free discharge limit. Especially the color, even the low concentration wastewater is highly colored but the discharge regulation says wastewater to be discharged should be colorless. Generally the result of the characterization shows that dye house wastewaters are hazardous and have to be treated before discharge.therefore due to this the dye section textile waste water was treated by produced silica gel to observe the optimum condition effects on waste water.

The methylene blue MB of the raw wastewater generated from companies dye section was 14.81465 mg/L. Results obtained after adsorption gave 84.62% reduction efficiencies in MB levels However, despite these reduction efficiencies, the resulting MB values less than the limits of effluent discharge of 2.278mg/L.The optimum prediction condition is validating.

Chemical Oxygen Demand is the measure of oxygen equivalent of the organic content of the sample that is susceptible to oxidation by a strong chemical oxidant. It is an evaluation used to

measure the level of water contamination by organic matter (Sulaiman, A.A. et al.,2016). The COD value is usually higher than the BOD because some organic materials in the water that are resistant to microbial oxidation and hence not involved in BOD could be easily chemically oxidized. COD measurements can be made in a few hours while BOD measures usually take five days (BOD_5) (Ram, S.L. et al., 2011). The use of low- cost adsorbent such activated carbon in waste water treatment plant has been found to increase COD removal efficiency (El-Dars, F.M.S.E.et al., 2014).due to this the produced silica gel has been reduced amount of COD after adsorption. The COD of the raw wastewater generated from companies was 506.8mg/L. Results obtained after adsorption gave 10% reduction efficiencies in COD levels of dye waste water used in Companies. However, despite these reduction efficiencies, the resulting COD values greatly exceeded the limits for effluent discharge. The presence of oxidizable inorganic compounds like extenders, pigments and additives were accountable for the high concentration of chemical oxygen demand in the samples.

BOD is the amount of oxygen utilized by microbial organisms to decompose organic compounds in water. The higher BOD concentration, the greater the extent of oxygen depletion in the water bodies. This results in the reduction of oxygen available for higher forms of aquatic life which consequently leads to the death of aquatic organisms (Rachna, B.2016). The adsorption of the waste water has not been reducing the BOD in waste water which means this process need biological method. TS and TSS also has not been shown significant change during the process of dye removal.

Chapter Five

Conclusion and Recommendation

5.1 Conclusion

This work was undertaken in order to exploit the the municipal solid waste bottom ash for the preparation of silica gel and to study their potential retention of a cationic dye (methylene blue, MB).The use of bottom ash as a precursor for the preparation of silica gel using NaOH as an extraction solvent chemical was analyzed in detail. The influences of several variables such as: extraction time, solid to liquid ratio and NaOH concentration at 75^0c extraction temperature. The experimental data showed that the maximum a purity was obtained and the optimization result shows that at 2M NaOH concentration, 2.5h extraction time and 1:1.5 solid to liquid ratio, can get 85.571% purity of silica gel.

The effects of extraction on silica gel purity properties were determined by $LiBO_2$ fusion, HF attack, gravimetric, colorimetric and atomic absorption spectrometer (AAS) of bottom ash composition before and after extraction, Fourier transform infrared (FT-IR). FTIR analysis identified the presence of siloxane and silanol groups, BET analysis to identified the gel surface area, pore volume and diameter. These siloxane and silanol groups may exercise a profound effect on the surface properties of silica gel and thus influence their adsorption characteristics. These groups have the potential active sites for the interaction with the adsorbate.

The purity analysis of silica xerogel that was analyzed by bottom ash composition showed high percentage of silca extracted (47.4%), some ions such as: 0.65% CaO, 0.74% Al_2o_3 and 0.22% iron, the purity of silica gel 84.1321%,the moisture content 5.26%,bulk density 0.73g/$cm^3$and The obtained gel is amorphous. Silica gel in the form of granulated, obtained at pH 3 (hydrosol), could reach a specific surface area up to 253.1m2/g. These characteristics display a very porous texture and, consequently, a great capacity of adsorption for this gel. Therefore based on the result of analysis the selected silica gel can be a good adsorbent with high surface area.

The dye removal performance of the silica gel on dye solution (synthetic waste water) determined with respect to contact time, MB concentration, and silica gel dosage. The results show that Optimum conditions are 30.85min 13.94mg/L, and 0.1g. Silica gel dosage for 86.101% dye removal efficiency with 0.99 of desirability. The overall results lead to conclude

that bottom ash can is converted into good adsorbents by optimum extraction for dye removal, and thus represent a waste minimization. Validation of the optimum condition of predicted were performed on textile waste water which has 14.81465mg/L dye concentration after adsorption it has 2.278 mg/L the error between the predictions and actual is 1.72%. Therefore, the removal efficiency of predicted model can satisfy the actual result. Generally utilization of bottom ash for the adsorbent preparation can also contribute waste minimization.

5.2 Recommendation

If some further research work is carried out to explore the potential of this bottom ash, recommended studies are listed below:

- ✓ From the result shows purity of silica gel reduced due to the remaining ions. Therefore, to get 94-96% pure silica gel Bottom ash needs further treatment before extraction of silica.
- ✓ Determination of the dye removal capacity using adsorption isotherm models and kinetic adsorption in order to examine the controlling mechanism of the adsorption process also suggested.

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Appendix A











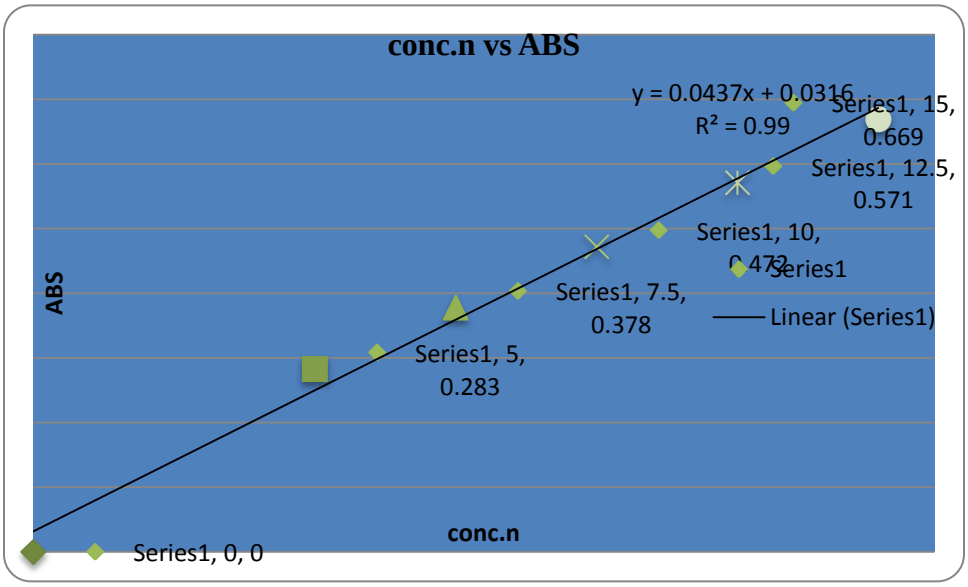



Appendix B

Methylene blue solution with different concentration

Test	ABS	CON.N
1	0	0
2	0.283	5
3	0.378	7.5
4	0.472	10
5	0.571	12.5
6	0.669	15

Calibration curve



Run no	A	B	C	Weight final	
1	2	2	2	0.1471	85.29
2	1	1	2	0.37573	62.427
3	3	1	2	0.35049	64.951
4	1	2	1	0.37421	62.579
5	1	3	2	0.34064	65.936
6	2	3	1	0.33505	66.495
7	3	2	3	0.18099	81.901
8	3	2	1	0.3505	64.95
9	3	3	2	0.2675	73.25
10	2	2	2	0.1456	85.44
11	2	1	3	0.23138	76.862
12	1	2	3	0.24614	75.386
13	2	2	2	0.1425	85.75
14	2	1	1	0.3451	65.49
15	2	2	2	0.1441	85.59
16	2	2	2	0.14249	85.751
17	2	3	3	0.14247	85.753

Where A:NaOH ,B: ratio and C time

Adsorption Experimental Analysis

	A	B	C	abso	Cf	R%
1	**15**	**15**	**0.05**	0.486648	10.413	30.58
2	15	15	0.15	0.205144	3.97125	73.525
3	30	15	0.1	0.1267	2.1762	85.492
4	15	10	0.1	0.198093	3.8099	61.901
5	15	20	0.1	0.346677	7.21	63.95
6	45	10	0.1	0.09483	1.4469	85.531
7	30	10	0.15	0.094895	1.4484	85.516
8	45	20	0.1	0.335315	6.95	65.25
9	30	15	0.1	0.129263	2.23485	85.101
10	30	15	0.1	0.12868	2.2215	85.19
11	30	15	0.1	0.134658	2.3583	84.278
12	45	15	0.15	0.126444	2.17035	85.531
13	30	10	0.05	0.276386	5.6015	43.985
14	30	20	0.05	0.637369	13.862	30.69
15	30	20	0.15	0.185774	3.528	82.36
16	45	15	0.05	0.43236	9.1707	38.862
17	30	15	0.1	0.12687	2.1801	85.466

Where A:contact time ,B: MB concentration ,C silica dosage and R:removal efficiency

BET TEST