DECLARATIONS
I hereby declare that this is my original work and has not been presented for the award of a degree in any other university.

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Reg. No. 156F/27069/2013

Signature .................. Date ..................................

SUPERVISORS’ DECLARATION
We confirm that the work reported in this thesis was carried out by the candidate with our approval as university supervisors.

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Signature .......................... Date ..........................
DEDICATIONS
I am proud to dedicate this work to the family of Alkali Danjuma Mustapha. I could not have completed this programme without their support, help, encouragement, sense of humor and prayers.
ACKNOWLEDGEMENT

I thank Almighty Allah (SWT) for inspiring my life, giving me strength, good health and sound mind to accomplish my studies. I sincerely thank my supervisors Dr. Harun Mbatha Mbuvi and Dr. Evans Changamu Ogwagwa both of Kenyatta University for their able, kind, consistent and constant educative guidance throughout my research.

I most sincerely thank the Water Resource Management Authority (WRMA) for allowing me to carry out part of my study in their central laboratory. I also take this opportunity to thank the Kenyatta University Chemistry Department staff and laboratory technicians for their support during my research.

Special thanks go to my friends at school and home like Engr Auwal I. Haruna, Haruna Tanko, Ibrahim H. Aliyu, Mu’azu Bala, Abubakar Chadi, Isah Mahmoud Mustapha, Abubakar Salihu, Umar Aliyu and Nura Musa Umar. May Allah reward you abundantly.


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# ABBREVIATIONS AND ACRONYMS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>APHA</td>
<td>American Public Health Associations</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transforms Infrared Spectroscopy</td>
</tr>
<tr>
<td>IEP</td>
<td>Isoelectric point</td>
</tr>
<tr>
<td>ISE</td>
<td>Ions selective electrode</td>
</tr>
<tr>
<td>$K_D$</td>
<td>Distributions coefficient</td>
</tr>
<tr>
<td>PAA</td>
<td>Polyacrylic acid</td>
</tr>
<tr>
<td>PZC</td>
<td>Point of zero charge</td>
</tr>
<tr>
<td>RGNDWM</td>
<td>Rajiv Gandhi national drinking water missions</td>
</tr>
<tr>
<td>RHA</td>
<td>Rice husk ash</td>
</tr>
<tr>
<td>SBA</td>
<td>Sugarcane bagasse ash</td>
</tr>
<tr>
<td>SCE</td>
<td>Standard calomel cathode</td>
</tr>
<tr>
<td>SNA</td>
<td>Silicon nitride A</td>
</tr>
<tr>
<td>SNB</td>
<td>Silicon nitride B</td>
</tr>
<tr>
<td>SNC</td>
<td>Silicon nitride C</td>
</tr>
<tr>
<td>SND</td>
<td>Silicon nitride D</td>
</tr>
<tr>
<td>TISAB</td>
<td>Total ionic strength adjustment buffer</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organizations</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray Fluorescence</td>
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ABSTRACT

High concentrations of fluoride in drinking water pose serious problems associated with dental and skeletal fluorosis to humans in several parts of the world. Among various methods used for defluoridation such as electrochemical degradation, ion exchange, precipitation coagulation, adsorption offers an attractive method for the removal of fluoride in terms of cost, simplicity of design and operations. Silicon nitride is a material that is characterized by high mechanical strength, thermal and chemical resistance. It also has high surface area with positive sites emanating from the silamine functional groups. Despite these excellent properties that make it a potential adsorbent for fluoride ions, no reports have been made on its use for this purpose. Therefore, the aim of this study was to synthesize, characterize silicon nitride from rice husk ash (RHA) and sugarcane bagasse ash (SBA) and to determine its adsorption capacity and efficiency for fluoride ions from aqueous media. The silicon nitride was synthesized by hydrothermal synthesis technique at four different temperatures, of 100°C, 150°C, 200°C and 300°C and labeled, SNA, SNB, SNC and SND respectively. The resultant silicon nitride samples were characterized by X-ray diffraction, X-ray fluorescence (XRF) and FTIR spectroscopy. FTIR spectra suggested that the compounds prepared had similar functional groups. The X-ray diffractogram show that SNA contained 64.6% α-phase and 27.8% β-phase silicon nitride. The adsorptions capacities and efficiencies were determined through batch experiments under various conditions of temperature, pH, adsorbent dose, initial fluoride ions concentration, contact time and shaking speed. The adsorptions capacities of silicon nitride samples were found to be 7.9, 8.9, 13.9 and 49.8 mg/g for SNA, SNB, SNC and SND, respectively. Optimum adsorptions capacities were achieved at pH 2 for SNA, SNB, SNC and pH 5 for SND, contact time of 100 minutes, temperature 25°C and shaking speed of 600 rpm. The adsorption data best fitted the Langmuir isotherm. This results indicate that the silicon nitride constitute a promising material for the development of an adsorption technology for the removal of fluoride ions from aqueous systems.
CHAPTER ONE
INTRODUCTION

1.1 Background information

Fluoride ion contamination of ground water has been recognized in numerous parts of world (Susheela, 1999). The common source of fluoride ion contamination is soil and rock arrangement such as fluorapatite, fluorspar and amphiboles, geochemical stores, normal water system and earth crust (Shailaja and Johnson, 2007). Waste water containing high measures of fluoride ions are generated by warm power plants, rubber, glass, fertilizer, ceramic productions, and electroplating industries (WHO, 1997). Fluoride ion concentrations in water are constrained by fluorite solubility, so that in the absence of dissolved calcium, higher fluoride solvency should be expected in ground water of areas where fluoride bearing minerals are common and vice versa (Edmund and Smedley, 1996).

Fluoride ion is viewed as helpful at optimum levels. It is vital for the strength of bones and teeth. Fluoride expands tooth mineralization and diminishes dental veneer demineralization and dentine touchiness (Basu et al., 2012). On the other hand at elevated amount it leads to mottling and embrittlement of teeth, a condition called dental fluorosis. Bones get to be denser, harder and weaker. Extended exposure of fluoride ions at certain level lead to skeletal fluorosis (Dissanayake, 1991). The World Health Organization (WHO) recommended the highest admissible limit of fluoride ions to be 1.5 mg/L in
drinking water while the acceptable fluoride ions concentrations lies in the range of 0.5 - 1.5 mg/L according to the APHA models (Basu et al., 2012).

Several physio-chemical techniques, such as adsorption, biodegradation, electrochemical degradation, ion exchange, precipitation coagulation, have been applied to remove fluoride ions from aqueous systems (Chen et al., 2011). Among these technologies, adsorption technology is the most cost-effective, eco-friendly and very simple (Ranjan et al., 2009). Among all types of conventional and non-conventional adsorbents, there has been an increase in the use of numerous waste materials like fly ash (Chidambaram et al., 2003), wood ash (Makhado et al., 2006), tea ash (Monadal et al., 2012), different coal-based adsorbents (coke, bituminous coal, Lignite, fine,) (Sivasamy et al., 2001), bagasse and cotton jute carbon (Jamode et al., 2001), rice husk, egg shell powder (Bhaumik et al., 2012), as adsorbents for removal of fluoride ions from aqueous solutions.

The preparation of silicon nitride (Si₃N₄) from RHs was initially reported in a US patent in 1974 (Cutler, 1974) where the reaction temperature was somewhere between 1100°C and 1350°C. Silicon nitride powders could be prepared up from RHs at temperatures somewhere around 1260°C and 1500°C under a nitrogen (ammonia) atmosphere. In the process of nitridation of rice husks, the abundance of carbon has been shown that could speed up the reaction rate and the molar proportions of C to SiO₂ is 2 (Komeya and Inoue, 1975; Liou and Chang, 1995). Similarly, Chen (2008) used rice husk in the synthesis of silicon nitride and silicon carbide by hydrothermal process. In this study, rice
husk ash was used as a source of silica, sugarcane bagasse as a source of carbon and aqueous ammonia as source of nitrogen in the synthesis of silicon nitride by hydrothermal process.

It is well known that silicon nitride forms the same type of surface hydroxyl layer as silica in aqueous solutions (Busca et al., 1986). However, there is a difference in the surface group composition. Unlike silica (Isoelectric point (IEP) of 2.2), silicon nitride exhibits an IEP of about 5.8. This difference is explained on the basis of the relative number of silanol (Si-OH) and amine (Si$_2$=NH) groups on the silicon nitride surface as compared to only silanol groups on silica surface (Bergstrom and Bostedt, 1990). The silanol groups are acidic in nature and thus result in a lower IEP, while the presence of amine groups being basic, results in a higher IEP.

Based on potentiometric titration, the surface site densities of amine group (Si$_2$=NH) and that of silanol group (Si-OH) are 0.56 /nm$^2$ and 1.83 26 /nm$^2$ respectively, on the silicon nitride surface (Sonnefeld, 1996). The density of silanol group on silica surface was estimated to be 0.74 /nm$^2$ (Sonnefeld, 1993). From these values, converted area of amine and silanol groups for molecular adsorption is 1.79 nm$^2$ and 0.546 nm$^2$, respectively on the silicon nitride surface, and area of silanol groups on silica was 1.35 nm$^2$ (Sonnefeld, 1996). These surface groups can acquire charge in aqueous solution according to the following chemical equations:
The adsorption density on Si₃N₄ was higher probably due to more positive sites on silicon nitride from amine groups. Si₃N₄ powder is produced mainly by carbothermal nitridation of silica (SiO₂) (Dijen and Vogy, 1992).

However, despite the extensive studies, the productions of silicon nitride from RHA has not been commercially implemented because of the problems associated with impurities as well as the long reaction time required (Riley, 2000). Synthesis of the α-phase is improved by increasing the partial pressure of CO in the vicinity of the sample (Alcala et al., 2002). Unpublished results from group members indicate that in the process of synthesizing silicaluminophosphates, 13% of the product was silicon nitride by XRD.

Literature has shown that polyacrylic adsorbed onto the negatively charged silicon nitride surface results in an increased repulsive surface potential. It is suggested that Polyacrylic acid (PAA) adsorbs onto silicon nitride by sequential adsorption of neighbouring segments (zipping) resulting in flat conformations. The total amount of amino acid adsorbed on the surface of silica and silicon nitride depends on the surface charge and the surface area available for adsorption (Suphantharida and Osseo, 2004). Most simple univalent electrolytes behave indifferently towards the Si₃N₄ surface, with the exception of fluoride which specifically adsorbs and may form a strong complex with surface silicon locales (Hackley and Malghan, 1994). The aim of this study was to synthesized
silicon nitrides ($\text{Si}_3\text{N}_4$) from rice husk ash, sugarcane bagasse ash and investigate its potential for removal of fluoride ions from aqueous solutions.

### 1.2 Statement of problem and justifications

More than a quarter of the world's populations will be residing in regions that are experiencing clean water scarcity as we approach the next century (Rosegrant et al., 2002). Good sanitation systems and clean water supply are considered to be the most important factors in ensuring good health in a community (Fewtrell et al., 2005). Rajiv Gandhi National Drinking Water Missions (RGNDWM) distributed a report in 1998, which demonstrated that the villagers in 8700 towns were taking contaminated ground water with high fluoride level (1.0 to 48.0 mg/L) and are under serious health risk. Epidemiological studies show that drinking water is the major source of fluoride daily intake and ceaseless utilization of drinking water with elevated fluoride ion concentrations ($>1.5$ mg/L) can incite birth, reproduction and immunological imperfections as well as dental and skeletal fluorosis. In Kenya, studies have reported high prevalence of fluorosis by the regions with Central (57%), Eastern (47%), and Rift Valley (34-80%) regions being the most affected. In such areas, fluorosis is a major impediment to water supply programmes and to the expansion of water-related economic programmes (Kiundi, 2010). The menace has been in existence for more than a decade and no solution seems to have been found to curb it. Numerous ways have been used to remove fluoride ions from waste water but still the problem has not been eradicated. Adsorption offers an attractive method for the removal of fluoride ions in terms of cost, simplicity of design and operations. Rice husk has been used to produce silicon nitride
but it lacks adequate carbon, to serve as the oxygen sink by forming CO gas and reduce the oxygen content on the powder surface. Silicon nitride is a material that possesses not only high mechanical strength, thermal and chemical resistance but also high surface area with positive site from the silamine group. Silicon nitride is known to adsorb some organic compound such as polyacrylic acid (PAA) and some amino acids. Due these excellent properties, it is expected to be a good candidate as an adsorbent for fluoride ions. So far not much researches have been done on the use of silicon nitride in contaminated water treatment in Kenya. Result from this study will form the basis for extended research into the use of local materials in the synthesis of silicon nitride for water treatment for local consumption in areas with high fluoride ions contamination.

1.3 Hypothesis

Silicon nitride synthesized from rice husk and sugarcane bagasse has adsorption capacity and efficiency for removal of fluoride ions from contaminated water.

1.4 Objectives

1.4.1 General objective

To synthesize silicon nitride from rice husk and sugar cane bagasse and assess its potential to remediate water from fluoride ion contamination.
1.4.2 Specific objectives

(i) To synthesize and characterize silicon nitride from rice husk ash (source of SiO$_2$) and sugarcane bagasse ash (source of carbon) at varied temperature.

(ii) To determine its adsorption capacity for fluoride ions from contaminated water.

(iii) To probe the efficiency of fluoride ions removal from contaminated water under various conditions.

(iv) To determine the adsorption optimum including, pH, adsorbent dose, contact time, shaking speed, temperature and initial ion concentration.

1.5 Significance of the study

The data obtained from this study is likely to change the way rice husk and sugarcane bagasse are treated. Positive adsorption results will mean an adsorbent obtained from agricultural waste namely rice husk and sugarcane bagasse will have been created.
CHAPTER TWO

LITERATURE REVIEW

2.1 Water pollution

Any adjustment in the biological, chemical and physical properties of water that harmfully affects living things is referred to as 'water pollution' (WHO, 1997). It is the next vital environmental issue after air pollution. As a result of the undesirable human exercises, water pollution is a developing danger in numerous nations. A more genuine part of water-pollution is what is created by human actions, and industrializations (Park, 2009). Infections spread through utilization of polluted water. It has been estimated that 50,000 individuals die daily as a result of water-related diseases (Nevondo and Cloete, 1999).

2.2 Fluorides

Fluoride compounds are salts that form when the element fluorine, joins with minerals in soil or rocks. Fluoride compounds such as: fluorosilicates and sodium fluoride leach easily into ground water as it travels through pores and spaces between rocks. Other than drinking fluoridated water, there are also different ways through which individuals are exposed to fluoride ions. Other sources of fluoride ions include food and beverages prepared using fluoridated water (Hileman, 1999), fluoridated dental items (Barot, 1998), mechanically deboned meat (Fein and Cerklewski, 2001) and pesticide deposits (e.g., from cryolite) on food (Barbier, 2010). Cryolite is basically responsible for the fluoride contaminations of our vegetables, organic products, natural product beverages and wine. It is splashed on grapes, potatoes and citrus natural product (Barbier, 2010).
The primary pathways by which people get exposed to excessive fluoride ions is by constant consumption of high fluoride water, when safer drinking water source are not readily accessible (Masearehas, 2000). Natural water is usually linked with excessive fluoride levels occur in calcium-deficient groundwater aquifers, in geothermal springs, and in certain sedimentary drainage basins (Teutli-Sequeira et al., 2001). The level of fluoride ions in drinking water, which are recommended by World Health Organization (WHO) are 0.7 mg/L (Disease control and prevent (CDC), 2005) and close monitoring of fluoride ions content of community water is highly recommended.

In Kenya, widespread endemic forms of fluoride are found, traditionally, in the rural areas along the volcanic belt associated with the great East African Rift Valley (Moturi, 2004). However, latest evidence has also revealed that the riparian community along the shores of the Lake Victoria could be at risk of severe forms of fluorosis and related fluoride toxicities due to excessive fluoride ions in their household water sources (Wanbu et al., 2014). In all cases, children under the age of 8 years are the most affected by all forms of fluorosis (Kahama et al., 1997). Prevention by way of controlling exposure to excessive fluoride ions through drinking water remains the most effective way of combating fluorosis in the communities. Because it is not normally feasible to change water source for the entire community, deflouridation of existing water source to remove excessive fluoride while leaving adequate level of fluoride to guard dental caries appear to be economically, the most feasible options (Wanbu et al., 2014).
2.2.1 Effects of fluoride

Sufficient dietary levels of fluoride ions are required for the development of healthy bones and teeth (Dean and Elvove, 1936). Fluoride ions deficiency increases teeth decay and prolonged exposure above optimum fluoride levels have detrimental health effects (Boldaji et al., 2009). The negative health effects of prolonged exposure to excessive fluoride ions may include mild colorization of teeth surface, staining, pitting and loss of the teeth enamel but severe crippling skeletal deformations and death may result in chronic cases (Wanbu et al., 2013). Non-skeletal adverse effect of excessive consumption of fluoride ions range from kidney, neurological, endocrine, thyroid and liver disorders to chronic disruptions of metabolic processes when the dosage is high (Ayoob and Gupta, 2006). Nonetheless, fluorosis remains the most noxious effect of long-term exposure to excessive dietary fluoride (Susheela et al., 1999). Children up to age 8 years, in whom teeth and bones are still developing, are most liable to the types of fluorosis. The condition cannot be changed and cure; once it develops it cannot be reversed.

Fluoride interacts with various enzymes (Carlsson, 1978). In blend with aluminum, fluoride interacts with guanosine nucleotide-restricting proteins (a group of proteins required in transmitting signals from a variety of stimuli outside a cell into the cell). Such communications give aluminum-fluoride buildings the possibility to interfere with signs from development factors, hormones and neurotransmitters (Kishi and Ishida, 1993).
2.3 Rice husk

Rice (*Oryza sativa*) is a major source food in majority of the developing nations. Rice husks (RH), also called as rice hulls, figure 2.1, serve as defensive cover of individual rice grains, which are expelled during the production of consumable rice. Approximately 20% of paddy weight is husk and rice generation in Kenya is approximated to around 110,000 metric tonnes (Giddel and Jivani, 2007).

![Rice husk](image)

**Plate 2.1: Rice husk**

Rice husk has to a great extent been considered as a waste material that is regularly burnt or dumped on landfills. Other than some low esteem applications, for example, feeding of cattle, land filling, building material, and protection material in homesteads and smoldering as fuel, the endeavors in making use of rice husks are constrained. This restriction is because of its extreme, massive and rough nature, low nutritional properties, imperviousness to degradation and high powder content. Consequently, rice husks are essentially left as agricultural waste or smoldered, which causes genuine capacity and
transfer issues in addition to environmental contamination (Giddel and Jivani, 2007). Dry rice husk contains 70–85% of natural matter (lignin, cellulose and sugars) and the rest is silica, which is available in the cell membrane (Vempati et al., 1995). In the past few decades, rice husks picked up fame for specialists on account of its high SiO$_2$ content, which have altogether enlarged the utilization of rice husks. At present, rice husks can be utilized as crude materials for the generation of silicon, silica, silicon carbide, silicon nitride, silicon tetrachloride and zeolite (Baris, 2014).

2.3.1 Composition of rice husk

Rice husks are made of organic and inorganic parts. The organic part, which is around 72% of the husk by weight, is chiefly made of lignin, cellulose, pentosans and other natural organic matter. The table below shows data on the natural constituents of the rice husk (Sharma et al., 1984).

**Table 2.1: Organic constituent of rice husks**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ cellulose</td>
<td>43.30</td>
</tr>
<tr>
<td>Lignin</td>
<td>22.00</td>
</tr>
<tr>
<td>D-xylose</td>
<td>17.52</td>
</tr>
<tr>
<td>L-arabinose</td>
<td>6.53</td>
</tr>
<tr>
<td>Methylgluconic acid</td>
<td>3.27</td>
</tr>
<tr>
<td>D-galactose</td>
<td>2.37</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>94.99</strong></td>
</tr>
</tbody>
</table>
The inorganic part, which forms ash after smoldering, is predominantly made of SiO$_2$ (87 to 97 wt%) and some impurities which are metal-oxides, for example, CaO, Fe$_2$O$_3$, MgO, Al$_2$O$_3$ (Chandrasekhar, 2003; Kurama and Kurama, 2003). The composition of rice husks depends on the region and sample. The explanations behind the compositional variety could be climatic and soil condition, crop year, soil science, substance composts utilized and sort of paddy. Based on literature (Govindarao, 1980), every reported data on the chemical analysis of rice husks from various regions of the world were considered and it was computed that 20 wt% ash, 22 wt% lignin, 38 wt% cellulose, 18 wt% pentosans and 2 wt% other natural matter were available in rice husks on a dry basis as an average (Chandrasekhar, 2003).

2.3.2 Applications of rice husk

Rice husks can be used directly with no treatment for low value applications. These incorporate power, dairy cattle feeding, land filling and protection materials. However, rice husks are known to have a low calorific value of around 3585 kcal/kg and high ash content. This makes it less desirable as a fuel (Genieva et al., 2008). Likewise rice husks being fibrous materials can prove to be fatal for the cattle feeding. Utilization of rice husk or its fiery ash in area filling is likewise an ecologically perilous ways of using waste (Giddel and Jivani, 2007).

Rice husks are basically considered as crude materials for the generation of nonconventional materials. It was expressed before that rice husk contain both silica and carbon and thus, it is a possible candidate for the carbothermal production of silicon
nitride. One major advantage of using rice husks is that, silica and carbon present in the husk is already in intimate contact and homogeneously mixed with high specific surface area (Sun and Gong, 2001). This would influence the response energy in a positive way and cause the reaction to happen more effortlessly than the mechanical blending of commercial silica and carbon powders. On the other hand, rice husks usually contain high amounts of impurities, which ends up affecting the product properties and/or produced phases.

2.4 Sugar cane bagasse

Sugarcane (*Saccarum officinarum*) bagasse is a fibrous waste delivered in huge amounts by sugarcane processing. In general, 1 ton of sugarcane generates 280 kg of bagasse, the stringy by-item staying after sugar extraction from sugarcane (Sun *et al*., 2004). The use of sugarcane bagasse is still restricted and is principally utilized as a fuel to control the sugar factories (Antaresti *et al*., 2002). Sugarcane enterprises deliver a lot of bagasse that is smoldered to create vitality to sugar processes yet at the same time huge amount are left unused. Sugarcane bagasse contains 50% cellulose, 27% hemicellulose and 23% lignin (Manish *et al*., 2013). Sugarcane bagasse contains 9.78 % of silica and 90.22 % of carbon, as compare to rice straw which contains 36.14 % of silica and 63.86 % of carbon (Suhardy *et al*., 2007).
Plate 2.2: Sugarcane bagasse

2.5 Silicon nitride

Silicon nitride is non-oxide basic material, which has been known for roughly hundred and fifty years. It is a decent material for different applications because of its numerous magnificent high temperature, high quality and hardness, and imperviousness to creep, oxidations, and warm shock (Komeya and Inoue, 1975) this makes it desirable material for investigations. So results of Si₃N₄, including motors and turbine cutting edges, typically connected on the raised temperature.
Silicon nitride $\text{Si}_3\text{N}_4$ exists in two hexagonal crystallographic forms which are characterized as $\alpha$-$\text{Si}_3\text{N}_4$ and $\beta$-$\text{Si}_3\text{N}_4$ (Riley, 2000; Roberts and Covington, 2005). The crystallographic information’s is shown in table 2.2.

**Table 2.2: Some crystallographic data of silicon nitride**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>Lattice parameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-$\text{Si}_3\text{N}_4$</td>
<td>Hexagonal</td>
<td>$a = 0.7748$, $c = 0.5618$</td>
</tr>
<tr>
<td>$\beta$-$\text{Si}_3\text{N}_4$</td>
<td>hexagonal</td>
<td>$a = 0.7608$, $c = 0.2911$</td>
</tr>
</tbody>
</table>

Every silicon atom is at the focal point of a tetrahedron and every nitrogen atom is in trigonal and roughly planar coordination by three silicon atoms, in order to connect three $\text{SiN}_4$ tetrahedra.
This rigid structure and strong covalent bonds are the reason for the remarkable hardness, and mechanical properties of this material (Lange et al., 1991; Riley, 2000). The precious stone structure of $\alpha$-$\text{Si}_3\text{N}_4$, as shown in Figure 2.2 was resolved to be firmly identified with that of $\beta$-$\text{Si}_3\text{N}_4$, comprising of interchangeable basal layers of $\beta$-$\text{Si}_3\text{N}_4$ and a mirror image of $\beta$-$\text{Si}_3\text{N}_4$, which results in the multiplied c-axis measurement contrasted with $\beta$-$\text{Si}_3\text{N}_4$. It has a unit cell composed of $\text{Si}_{12}\text{N}_{16}$ under the space bunch $P_{31c}$. In spite of the fact that the $\beta$-structure is just strain free, the $\alpha$-structure contains extensive strain, which is communicated by the cross sections twisting and the relocations of atoms from the admired positions (Riley, 2000). The bond lengths in the $\alpha$-$\text{Si}_3\text{N}_4$ structure are uncertain and they shift a great deal more so than in the $\beta$-$\text{Si}_3\text{N}_4$. There is existence of little varieties in the unit-cell measurements of materials got from various sources and with various molecule morphologies (Lange et al., 1991; Riley, 2000).
The precious stone structure of $\alpha$-Si$_3$N$_4$ is extremely unpredictable. Upon studies, it is inferred that $\alpha$-stage has a scope of homogeneity. This can be clarified by an imperfect structure as appeared in figure 2.2 with roughly 25% nitrogen opening in the N(4) destinations and incomplete substitutions of nitrogen by oxygen in N(1) sites with electrical lack of bias being acquired by a proper number of silicon vacancies or Si$^{3+}$ species. Also, $\alpha$ to $\beta$ change just happens at temperatures more prominent than 1650$^\circ$C. Apparently for dynamic reasons, $\beta$ to $\alpha$ change has not been studied yet, but it would be expected to be too slow to detect at temperatures lower than 1400$^\circ$C (Lange et al., 1991; Riley, 2000).

2.5.1 Physical properties of silicon nitride

In the generation of advanced ceramics, utilization of various strategies and even little varieties in the control of parameters influencing these procedures result in various properties in the final products. This scatter in the property information is for the most part because of the beginning powder attributes (size, purity, shape, and so on), sum and sort of sintering added substances and covers, powder forming and sintering procedures, temperature, weight and dousing time during sintering, which influences a definitive microstructure in the item (Lange et al., 1991). This can be ascribed to the complex microstructure and the troubles in fitting it (Hoffmann, 1998).
Table 2.3: Physical properties of silicon nitride material (Lange et al., 1991)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decompositions temperature (K)</td>
<td>2173</td>
</tr>
<tr>
<td>Theoretical density (g/cm$^3$)</td>
<td>α-phase: 3.168 - 3.118</td>
</tr>
<tr>
<td></td>
<td>β-phase: 3.19 - 3.202</td>
</tr>
<tr>
<td>Material density (g/cm$^3$)</td>
<td>95 – 100% theoretical density</td>
</tr>
<tr>
<td>Thermal expansions coefficient (293-1473K) (K$^{-1}$)</td>
<td>2.9-3.6×10$^{-6}$</td>
</tr>
<tr>
<td>Specific Heat (J/kgK$^{-1}$)</td>
<td>700</td>
</tr>
<tr>
<td>Electric resistance (Ωcm)</td>
<td>$10^{13}$</td>
</tr>
<tr>
<td>Microhardness (Vickers)(MNm$^{-2}$)</td>
<td>1400 – 1700</td>
</tr>
<tr>
<td>Bending strength (MPa)</td>
<td>600 – 1000</td>
</tr>
<tr>
<td>Fracture toughness (MPaM$^{1/2}$)</td>
<td>5-8</td>
</tr>
<tr>
<td>Elasticity modulus (GPa)</td>
<td>280 – 320</td>
</tr>
<tr>
<td>Critical temperature difference in Thermal shock (K)</td>
<td>600 – 800</td>
</tr>
<tr>
<td>Thermal conductivity (Wm$^{-1}$ K$^{-1}$)</td>
<td>15 – 30</td>
</tr>
</tbody>
</table>

2.5.2 Chemical properties

$\text{Si}_3\text{N}_4$ is an inert material with an extensive variety of liquid metals such as, Al, Zn, Sn, Pb, Cu, Ag and Cd. However when in contact with transition metals like Fe, Co, Ni, V and Cr, it reacts with the metal to form metal silicides and $\text{N}_2$. When it is in contact with liquid salts, oxidic slags, and glasses, the occurring corrosion is slow. Permeable $\text{Si}_3\text{N}_4$ parts are known not to be attacked by hot solid scathing solutions and melts with the development of $\text{NH}_3$ (Lange et al., 1991). Ability of $\text{Si}_3\text{N}_4$ to withstand high temperatures under oxidizing conditions without excessive oxidations therefore rests on the integrity and stability of the surface oxide layer (Riley, 2000; Somiya, 2003). It is realized that $\text{Si}_3\text{N}_4$ has a good oxidation resistance up to 1400°C, for the most part because of these defensive layers (Lange et al., 1991).
2.5.3 Applications of silicon nitride

The enhancements in the efficiency of heat motors by and large require the auxiliary materials to work under severe conditions. The turbine delta temperature of most progressive gas turbines has effectively far exceeded the softening purpose of the super compounds (Somiya, 2003). Si$_3$N$_4$ is the most suitable substitution of combinations concerning basic motor parts (Somiya, 2003). In the 300 kW-class, artistic gas turbine motor CGT301, which is created by Ishikawajima-Harima Heavy Industry in Japan for co-era use, Si$_3$N$_4$ was utilized as a part of the making of the sharp edges, spouts, heat exchanger, fuel spout, burning liners, nose cone, channel liner, inward ring, cover rings, holding rings and seal rings. Fruitful get together of Si$_3$N$_4$ based advanced ceramic material into CGT301 motor have empowered a high motor proficiency of 35% or more, which normally indicates productivity around 20% with metallic parts (Somiya, 2003). It is evaluated that more than 300000 sintered Si$_3$N$_4$ turbocharger rotors are made every year (Riley, 2000).

Another application zone of Si$_3$N$_4$, other than motor parts, is cutting tools. With its high heat resistance, high cutting velocity (up to 15 m/s), high wear resistance and concoction idleness, it has the required properties for making cutting devices. Unlike other cutting device materials like boron nitride and precious stone, the reduction in its small scale hardness quality is low above 1273 K, which makes it a reasonable material for cutting instrument, particularly for fast processing of cast iron (Somiya, 2003). Sintered Si$_3$N$_4$ cuts cast iron, hard steel and nickel-based compounds with surface paces up to 25 times those possible with customary materials, for example, tungsten carbide (Riley, 2000).
Application in which Si₃N₄ is utilized incorporate grating situations as a part of oil boring, vacuum pumps, and sterilizable and un-greased up dental drills (Riley, 2000). Si₃N₄ is additionally being utilized as a part of the making of artistic composites. SiC (molecule or bristle) Si₃N₄ composites/nano-composites show higher flexural quality at high temperatures up to 970 MPa at 1400°C (Somiya, 2003). Inside strung cover spouts for latent gas welding and cutting lights, thermocouple sheaths, thin films in microelectronics zone, dental porcelain terminating plate and backings are other applications territories where Si₃N₄ is utilized (Riley, 2000).

2.5.4 Methods of synthesizing silicon nitride

Si₃N₄ can be produced by an assortment of techniques depending on whether the last product is wanted to be a part, thin film or powder. A few strategies can be utilized reciprocally to deliver various types of items; however the vast majority of the techniques concentrate on the blend of Si₃N₄ powders which are to be further treated in powder based generations systems. Three most imperative strategies for Si₃N₄ blend are recorded as:

(i) Direct nitridation of silicon powders
(ii) Reactions of silicon compounds with ammonia and
(iii) Carbothermal reductions of silica within the sight of nitrogen (Lange et al., 1991; Kuskonmaz et al., 1996; Rahaman, 2006).
2.5.4.1 Direct nitridation

Direct nitridation of silicon is the most widely used method for the industrial synthesis of Si₃N₄ powders as reported by Lange et al. (1991). Depending on the silicon source, the purity of the product changes, thus high purity of silicon powders are desired for nitridation. For the synthesis of Si₃N₄ powders, piles of silicon powders are allowed to react with nitrogen in chamber or conveyor-type pusher furnaces for 10 to 30 hours at 1200 to 1400ºC (Lange et al., 1991; McColm and Clark, 1998);

\[ 3\text{Si} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4 \]  
\[ G^\circ (\text{KJ/mol}) = -723800 + 315.1 \times T \]

This method produces 100% crystalline product. Lower temperatures and mixture of hydrogen in the nitriding gas tend to form α-Si₃N₄, whereas higher temperatures tend to form β-Si₃N₄ (Lange et al., 1991).

2.5.4.2 Reactions of silicon compounds with ammonia

This technique can be partitioned in two sections as liquid stage reaction and gas-stage reaction. For the liquid stage reaction strategy to create Si₃N₄ powder, which is otherwise called the imide precipitation technique, the reaction between fluid SiCl₄ and liquid NH₃ is utilized.

\[ \text{SiCl}_4(\ell) + 6\text{NH}_3(\ell) \rightarrow \text{Si(NH)}_2 + 4\text{NH}_4\text{Cl} \]  
\[ 3\text{Si(NH)}_2 \rightarrow \text{Si}_3\text{N}_4 + \text{N}_2 + 3\text{H}_2 \]
Heating at temperatures between 1200 - 1400°C favours the crystallization of α-stage joined by molecule coarsening. At temperatures above 1500°C, it yields β-phase (Lange et al., 1991).

2.5.4.3 Carbothermal reduction and nitridation of SiO₂

This technique utilizes a blend of SiO₂ and C powders at temperature of up to 1500°C in a N₂ environment. In light of the across the board accessibility of pure, fine and minimal effort SiO₂ and C powders, this technique is an alluring contrasting option to direct nitridation of silicon in the generation of Si₃N₄. This procedure has been utilized to create Si₃N₄ powders mechanically by Toshiba (Japan) (Lange et al., 1991);

\[ 3\text{SiO}_2(s) + 6\text{C}(s) + 2\text{N}_2(g) \rightarrow \text{Si}_3\text{N}_4(s) + 6\text{CO}(g) \]  

Generally SiO₂:C ratio of 1:2 to 1:10 by weight is utilized (Lange et al., 1991). The abundance of carbon is utilized as oxygen sink to form CO gas and diminish the oxygen content on powder surface. After nitridation, any unreacted carbon must be removed in an oxidizing environment, which may bring about some re-oxidations of Si₃N₄ surfaces (Rahaman, 2006).

The CO formed over the span of reactions must be expelled from the system in order to prevent the opposite reaction. Consequently, CO partial pressure must be kept low by a stream of N₂. Si₃N₄ arrangement is improved at higher temperatures, however at temperatures above 1450°C, SiC additionally begins to form, which is for all intents and purposes conjoined from Si₃N₄. Molecular size and morphology can be changed by
including round or stubble type Si₃N₄ to the starting mixture. Molecular size of carbon additionally influences Si₃N₄ powder properties since it goes about as a nucleation focus in the Si₃N₄ arrangement. Fine and high particulate surface area carbon powder improves the arrangement of circular Si₃N₄ particles, however coarse and low particulate surface zone carbon powders support stubble Si₃N₄ (Lange et al., 1991). Unreacted carbon and unreacted SiO₂ can be expelled from the item by heating under air around 600-800°C and HF draining, respectively (Lange et al., 1991).

2.5.4.4 Other techniques used for Si₃N₄ synthesis

(a) Vapour phase reactions of silicon halides or silane:

\[ 3\text{SiCl}_4 + 16\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{NH}_4\text{Cl} \]

2.5

\[ 3\text{SiH}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{H}_2 \]

2.6

(b) Warm disintegrations of silicon amide or imide

\[ 3\text{Si} (\text{NH})_2 \rightarrow \text{Si}_3\text{N}_4 + 2\text{NH}_3 \]

2.7

\[ 3\text{Si} (\text{NH}_4)_2 \rightarrow \text{Si}_3\text{N}_4 + 8\text{NH}_3 \]

2.8

But these either require expensive equipment or elevated temperature (for NH₃ can corrode the equipment).

2.5.5 Silicon nitride in aqueous solution

The electric charges give electrostatic adjustment in aqueous suspensions promoting the advancement of a double layer. The solid surface reaction of Si₃N₄ with H⁺ and OH⁻ in water includes distinctive sort of collaborations, for example, the formations of silica and
silanols, alkali and amine related reactions and disintegrations and re-adsorptions of contaminations (Malghan, 1992). The predominant species coming about because of this reaction are \( \text{SiOH}^+ \) and \( \text{Si}_2\text{NH}_2^+ \) for pH lower than the IEP and \( \text{SiO}^- \) and \( \text{Si}_2\text{N}^- \) for pHs higher than the IEP.

Busca et al. (1986) published an extensive study of the surface properties of a high surface area silicon nitride which was prepared by nitridation of amorphous silica with ammonia at 1300°C. The presence of SiOH (surface silanol), Si-NH-Si (imido group) and SiH (silane) was observed as well as evidence of basic nitrogen bonded to three silicon atoms. They cite an increased basicity of silicon nitride with respect to that observed for silica. This is attributed to the presence of the imido and the basic nitrogen groups. In addition, they also report a slight reduction in the acid strength of the silanol group on silicon nitride, as compared to silanol found on silica surface. The reduction in the silanol acidity is attributed to the smaller effect of nitrogen in silicon nitride bonds compared to oxygen in silica bonds. Busca did not observe any \( \text{Si}_2\text{NH}_2 \) (amido) group on the surface after vacuum pretreatment of the powder at temperature up to 400°C. Further evacuations and heating to 200°C -300°C condences the near lying hydrogen bonded silanol. After the initial activations of the amorphous silicon nitride (by evacuations at 400°C), Busca also noted that hydrogen bonded ammonia is completely desorbed by evacuations at room temperature.
2.5.6 Silicon nitride for adsorption

Silicon nitride has been used for adsorption experiments, most especially of organic compounds. A silicon nitride surface might have amphoteric silanol (SiOH) as well as basic primary, secondary, and tertiary amine groups (SiNH$_2$, Si$_2$NH, and Si$_3$N), (Bergstrom and Pugh, 1989). The total amount of amino acid adsorbed on the surface of silica and silicon nitride depends on the surface charge and the surface area available for adsorptions (Suphantharida and Osseo, 2004). At alkaline pH range of 9 to 11, surface charge of L-proline and L-Arginine are positive (Lehninger et al., 1993). Since the point of zero charge (PZC) of silica is nearly at pH 2.0 and that of silicon nitride at pH 7, both surfaces have negative charge in the alkaline pH range (Hegde and Babu, 2004). Hence, it is expected that the amino acids would be attracted by both the work surfaces. The adsorbed quantities (mmol/g) of amino acids is much less on silicon nitride surface when compared to silica surface, mainly because the surface area available is much more (380 m$^2$/g) for silica compared to silicon nitride (9.4 m$^2$/g).

The ionization chemistry of polyacrylic acid (PAA) was characterized by the potentiometric titration method. In general, the amount that is adsorbed increases as the polymer concentration increases, until a plateau region is reached. The isotherms for pH 3 can be described as high affinity and are characterized by strong adsorptions and apparent surface saturations. Adsorption capacity increased significantly as the value of relative molecular mass increased at the low pH value but was roughly independent of relative molecular mass above pH 5; this suggests that, in the partially or fully ionized
form, adsorption of PAA was dominated by electrostatic interactions between the ionized sites on the polymer and the surface-charged sites on the solid.

The measure of NH$_4$PA adsorbed on the Si$_3$N$_4$ powder diminished with increasing pH. This is comprehended to be as result of the electrostatic repulsions between the negatively charged Si$_3$N$_4$ powder and the anionic polymer. This adsorptions behavior is not of “high-affinity type (Casarano and Aksay, 1988). The more prominent measure of NH$_4$PA adsorbed added an expansions of the negative net surface charge (NH$_4$PA adsorbed Si$_3$N$_4$/sintering help particles), (Albano and Garrido, 1998). Therefore, the abatement in the slip consistency regarding Si$_3$N$_4$ slips with NH$_4$PA at the same pH was ascribed to the upgraded electrostatic repulsions between ions. Notwithstanding the electrostatic connections, the steric cooperation of the adsorbed polyacrylate has a positive commitment to the scattering (Liu and Malghan, 1996).

Beside the sign of surface charge, hydrogen bonding plays an important role in adsorptions of organic molecules on silicon nitride, benzoic acid and benzyl amine prefer to adsorb in the basic amine (Si$_2$NH) group through hydrogen bonding (N-H).

2.6 Various technologies for fluoride removal

2.6.1 Membrane process

The membrane separations process is much more well-known from industrial viewpoints for defluoridation of groundwater, wastewater treatment and sea water desalinations (Maheswari and Hoelzel, 2002). In a membrane separation process, particles are isolated
on the premise of their molecular size and shape with the utilization of extraordinarily composed semi-permeable membrane. The semi-permeable membrane is frequently a thin, nonporous or porous polymeric film, ceramic, or metal material or even a liquid or gas. The membrane must not dissolve, disintegrate or break (Seadar and Heneley, 2005). The most normally utilized membrane separation processes for removal of fluoride are reverse osmosis, nano-filtrations, Donnan-dialysis and electrodialysis.

2.6.1.1 Reverse osmosis (RO)

Reverse Osmosis (RO) is a physical process in which the anions are removed by applying pressure on the feed water to direct it through the semi permeable membrane. RO works at higher pressure with more prominent rejections of dissolved solids. The membrane rejects the ions taking into account the size and electrical charge. More than 90% of fluoride can be removed regardless of initial fluoride concentrations using RO membrane separations process (Ndiaye et al., 2005).

Ndiaye et al. (2005) utilized RO separations process for defluoridation of industrial wastewater and noticed that the sending back of fluoride ions was regularly higher than 98%, considering that the RO membrane was completely recovered after every arrangement of analyses (Ndiaye et al., 2005). The study of Gedam et al. (2012) reported that 95 to 98% of fluoride was removed from ground water of Moradgaon village of Chandrapur district by using Polyamide RO membrane (Gedam et al., 2012).
2.6.1.2 Nano filtrations membrane process

Nano-filtration (NF) is the latest innovation among all the membrane processes utilized for defluoridation of water. The essential contrast between NF and RO membrane separations is that NF has somewhat bigger pores than those utilized for reverse osmosis and offer less resistance to entry of both solvent and solute. As a result, pressures needed are much lower, energy requirement are less, removal of solute is substantially less throughout, and flow rates are faster (Mohapatra et al., 2009). Nano-filtration membrane removes essentially the larger dissolved solids when compared to the RO making the process more prudent. Notwithstanding, the permeability of nano-filtrations membrane is higher than RO membrane, making the performance of NF in desalinations best for some brackish water (Lhassani et al., 2001). Diawara et al. (2011) observed that NF membrane has given a fluorine retentions rate differing somewhere around 63.3% and 71% in certain regions in Senegal (Assefa, 2006).

2.6.1.3 Dialysis

Dialysis isolates solutes by transport of the solutes through a film as opposed to use of a layer to hold the solutes while water goes through it as in reverse osmosis and nanofiltration. The film pores are significantly less restrictive than those for nanofiltration, and the solute can be driven through by either the Donnan impact or an associated electric field (Donnan, 1911). Concentration contrast is the most evident main thrust for particle transport in Donnan dialysis. A negative particle that can be driven out of a feed solution through Donnan dialysis is furnished with anions trade layer by using a second soluble stream. The concentration contrast of hydroxide ions between the two
solutions constrains the hydroxide ions to diffuse into food arrangement. This makes an oppositely coordinated electrical field driving an extraction of negative particles from the food solutions (Hichour et al., 2000). Hichour et al. (2000) analyzed the Donnan dialysis process in a counter current framework in which the anions-trade layer was stacked with sodium chloride and the food was 0.001M NaF together with other sodium salts. Fluoride relocated into the recipient as different ions moved into the food. This strategy was later used to defluoridate solutions made to retreat high fluoride Africa groundwater (>30mg/L fluoride) and whatever different ions were available the fluoride in the food could be brought below 1.5 mg/L (Hichour et al., 2000).

### 2.6.1.4 Electro-dialysis

Electro-dialysis is the removal of ionic components from aqueous solutions through ion exchange membranes under the driving force of an electric potential difference. Electro-dialysis is like reverse osmosis, except current, rather than pressure, to separate ionic contaminants from water. In any case, electro-dialysis is not suitable for rural use because it requires electricity. Adhikary et al. (1989) have treated defluoridation of brackish water having fluoride up to 10 mg/L with TDS up to 5000 mg/L with an energy necessity of < 1 KWh/Kg of salt removed and brought it to reasonable furthest reaches of 600 mg/L TDS and 1.5 mg/L fluoride. Amor et al. (1988) used electro-dialysis process to produce drinkable water from defluoridated brackish water containing 3000 mg/L of total dissolved solids (TDS) and 3 mg/L of fluoride.
2.6.1.5 Electro-coagulations (EC) process

Electrocoagulation is a technique that involves applying direct current to sacrificial electrodes that are submerged in an aqueous solution (Emamjomeh et al., 2011). In order to remove the flocculating agent produced by electro-oxidations of a sacrificial anode, electro-coagulation is a fast and efficient process, and generally made of iron or aluminum. This technique consolidates three fundamental associated processes, operating synergistically to remove pollutants: electrochemistry, coagulations and hydrodynamics. Electrocoagulations include electrolytic oxidations of a proper anode material. Electrocoagulations reactor is comprised of an electrolytic cell with one anode and one cathode (Mollah et al., 2001). Yang and Volesky (1999) studied the electrochemical removal of fluoride by delivering aluminium sorbent in a parallel-plate electrochemical reactor.

2.6.1.6 Adsorption process

Adsorption is the binding of molecular species from bulk solutions to a surface of a solid by physical or chemical forces. Adsorption procedures include the water’s entry through a contact bed where fluoride is removed by ion exchange or surface chemical reactions with the solid bed matrix. Adsorption is efficient and can remove ions over a wide range of pH (Das et al., 2005; Andey et al., 2013). Bone charcoal, activated soil sorbent, activated coconut shell powder, activated fly ash, activated alumina, activated carbon, activated alumina coated groundnut shell, coffee husk, rice husk, magnesia, serpentine, tri-calcium phosphate, defluoron-1, defluoron-2, silica gel, calcite, activated saw dust and so on, are various adsorbents reported in literature (Thergaonkar and Nawalakhe, 1971; Kariyanna, 1986).
The adsorption procedure can remove fluoride up to 90% and the treatment is exceptionally practical. Regeneration is needed at regular intervals of 4–5 months and viability of adsorbent for fluoride removal reduces after every regeneration cycle. Mckee and Johnston investigated the utilizations of powdered activated carbon for fluoride removal and accomplished noble outcomes (Mckee and Johnston, 1999).

2.7 Factors that affect adsorption processes

Numerous factors affect the adsorption ability of adsorbents during sorption process. Literature has shown that the effectiveness of adsorbents is highly impacted by factors such as, pH of solutions, temperature, shaking/agitations speed, contact time, adsorbent dose and concentrations of the ions (Nawar et al., 2013). These factors are discussed in the accompanying subsections.

2.7.1 Effect of pH

The degree of ionization of a species is affected by pH (for example, a weak acid or a weak basis). This in turn affects adsorptions (Azouaou et al., 2010). When the pH is altered, mineral surfaces become more positively charged with the increasing pH and the surface groups that have lost protons may be able to adsorb anions more readily, and cations less readily, from solutions (Singh et al., 2006). Control of pH therefore, is a major factor affecting defluoridation as well as the separations of ions from solutions containing different ions. The pH dependence occurs when the fluoride ions and hydroxyl ions compete for adsorptions site or when the ions and protons compete for the same active binding sites on the sorbent surface (Donmez and Aksu, 2002).
2.7.2 Effect of contact time

According to Yang and Volesky (1999), a large number of vacant surface sites are available for adsorptions during the initial stage and the solute concentrations gradient is high. With the passage of time, there is increase in the number of adsorption sites and the remaining vacant surface sites can easily be occupied due to strong forces between the solute molecules on the solid phase and in the bulk liquid phase (Yang and Volesky, 1999). The uptake is influenced by the speed at which the adsorbate is transferred from exterior to the interior sites of the adsorbent (Acksu, 2001).

2.7.3 Effect of agitations speed on adsorptions

Increment in the shaking rate expands the rate of the adsorptions. Higher mixing rates are expected to remove the film resistance that anticipates more ions to be adsorbed. At the point when the mixing rate is expanded the diffusion rate of the particles from the mass fluid to the fluid limit layer encompassing sorbent particles get to be higher in view of the upgrade of the turbulence and the abatement of the thickness of the fluid limit layer (Ghodbane et al., 2008).

2.7.4 Effect of adsorbent dose

This is the amount adsorbent brought into contact with the solute, the adsorption efficiency of an adsorbent increases with adsorbent dose (Xing et al., 2011). This is due to availability of more adsorption sites. However, the adsorption density reduces due to unsaturated adsorption sites. Adsorption density is also reduced due to particle interactions caused by high adsorbent concentrations.
2.7.5 Effect of temperature

Temperature has two principal impacts on the adsorption efficiency. Increasing the temperature is known to increase the rate of arrival of the sorbent inside the pores leading to diminishing of the solutions viscosity and in addition versatility (Aksu, 2001). The other impact is that equilibrium between the adsorbent and the sorbate is achieved inside a shorter time because of the expansions in the dispersions rate (Lodeiro et al., 2006). The effect of temperature on adsorptions likewise relies upon the warmth of sorption. More often than not for physical sorption, enthalpy of sorption is exothermic and favoured at lower temperature (Aksu, 2001).

2.7.6 Effect of initial ion concentration

Initial ion concentration significantly affects the adsorbent. As concentrations increase, there is an expansion in the number of ions bound yet the rate amount adsorbed diminishes. Increment in the measure of ions adsorbed with increase in concentrations has been ascribed to availability of binding site present on the sorbent (Mureithi et al., 2012).

2.8 Hydrothermal process of synthesis

The term "Hydrothermal" was utilized in 1849 by a British geologist, named Sir Roderick Murchison (1792-1871) (Chen, 2008). This procedure is normally done in fixed vertical autoclaves with temperature contrast (ΔT) arranged within the top and base of the vessel. Normally the supplement is put in the lower, more smoking part of the autoclave, and the seeds are mounted in the cooler upper part. Nowadays, the temperatures utilized are close
or even over the basic temperature (374.1°C) of clean water, which temperature the soaked vapour weight is 218.3 atm. The mineralizers utilized are basic (NaOH, KOH, Na₂CO₃, RbOH), these days, neutral materials (NH₄Cl, KF, CsF, NaCl, KCl, LiCl), and every so often corrosive arrangements (HCl, HI, H₂SO₄), are utilized. For the most part, expanding the concentrations of the mineralizer builds the solvency of the material being developed (Brice, 1986). The synthesis using hydrothermal method can be characterized as a strategy for blend of single crystals which relies upon the solubility of minerals in boiling water under high pressure. For this study, we chose the hydrothermal method because the high temperature can be replaced inside by pressure, so that to decrease the high energy required. Furthermore, we use the raw materials, rice hulls ash, ammonia and HCl as reactions materials, try to synthesize Si₃N₄ composite. Most important is its reactions temperature is between 200°C and 300°C.

2.9 Characterization techniques

Techniques for characterization are; X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infra-red (FTIR) spectroscopy, X-ray fluorescence (XRF), Thermo gravimetric analysis (TGA), Differential Thermal Analyses (DTA) among others. Techniques utilized in this study include X-ray diffraction (XRD) (Hemant et al., 2010; Ramaswamy et al., 2010). This gives the crystallographic basic status and periods of the whole part in a material. X-ray powder diffraction (XRD) is a systematic procedure used to recognize and portray obscure crystalline materials. XRD machine utilized as a part of this study was XRD (D2 Phaser Model-Bruker).
2.9.2 Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared spectroscopy (FTIR) is used mainly for functional group determination. The source of energy goes through an interferometer and onto the sample. IR light energy goes through a beam splitter, which sends the light in two headings at right points. One bar goes to a stationary reflect then back to the shaft splitter. Alternate goes to a moving mirror. The movement of the mirror makes the aggregate wavelength variable versus that taken by the stationary-mirror shaft. At the point when the two get together again at the shaft splitter, they recombine, however the distinctions in path lengths makes helpful and damaging interference. The recombined beam goes through the sample.

The sample ingests all the distinctive wavelengths normal for its range, and this subtracts particular wavelengths from the interferogram. The detector reports variety in energy versus time for all wavelengths at the same time. A laser shaft is superimposed to give a reference to the instrument operations. A scientific function called a Fourier transform permits us to change over intensity versus- time range into a power versus- recurrence range (Naja et al., 2005).
2.9.3 Ion selective electrode (ISE)

Ion-selective electrode (ISE) is otherwise called a specific ions electrode (SIE). It is a transducer that changes over the movement of ions dissolved in solutions into an electrical potential, which can be measured by a voltmeter or by a pH meter. The voltage is hypothetically subject to the logarithm of the ionic actions, as indicated by the Nernst conditions. The ISE can likewise be aligned to give readings of a specific ions present in a solutions in mg/L. The detecting part of the electrode that is plunged into the sample arrangement is normally made of an ion selective film.

2.9.4 X-ray fluorimetry

X-ray fluorimetry is a technique for the subjective and quantitative investigations of chemical elements (Mantler and Schreiner, 2000). It deals with wavelength dispersive spectroscopic rule (Johnson et al., 1999). When materials are presented to short-wavelength X-ray or to gamma beams, ionizations of their segment atoms happens.
Ionizations comprise of the launch of one or more electrons from the molecule, and may happen if the atom is presented to radiations with energy more prominent than its ionization potential (Young et al., 2010). X-rays and gamma rays can be sufficient to expel firmly held electrons from the internal orbitals of the atom (Drescher et al., 2002). The evacuation of an electron along these lines makes the electronic structure of the atom unsteady, and electrons in higher orbitals to fall into the lower orbital to fill the opening abandoned. In falling, energy is discharged as a photon, the energy of which is equivalent to the energy contrast of the two orbitals included. Therefore, the material discharges radiation, which has energy normal for the atoms present.

2.10 Adsorptions isotherms

An adsorptions isotherm is a curve relating the balance concentration of a solute on the surface of an adsorbent $q_e$, to the grouping of the solute in the fluid $C_e$, with which it is in contact. The adsorptions isotherm is additionally a condition relating the measure of solute adsorbed onto the solid and the balance concentrations of the solute in solutions at a given temperature. The most commonly utilized isotherms for wastewater treatment and activated carbon in water are the Freundlich and Langmuir isotherms (Oliveira et al., 2008).

2.10.1 Langmuir isotherm

The Langmuir isotherms portray quantitatively the development of a monolayer adsorbate on the external surface of the adsorbent, and after that no further adsorption
happens. Along these lines, the Langmuir represent the dispersions of ions between the solid and liquid stages (Vermeulan et al., 1966). The Langmuir isotherm is legitimate for monolayer adsorptions onto a surface containing a limited number of indistinguishable sites. The model assumes uniform energies of adsorption onto the surface and cancels transmigrations of adsorbate of the surface in the plane. Based upon these assumptions, Langmuir presented the following equation:

\[ q_e = \frac{Q_o K_L C_e}{1 + K_L C_e} \]  \hspace{1cm} 2.9

The linearizes Langmuir equation is presented as, in equation 2.10

\[ \frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{K_L Q_o C_e} \]  \hspace{1cm} 2.10

A plot of \( \frac{C_e}{q_e} \) against \( C_e \) gives a straight line from which \( Q_o \) and \( K_L \) can be obtained.

Where:

- \( C_e \) = the equilibrium concentrations of adsorbate (mg/L)
- \( q_e \) = the amount of ions adsorbed per gram of the adsorbent at equilibrium (mg/g).
- \( Q_o \) = maximum monolayer coverage capacity (mg/g)
- \( K_L \) = Langmuir isotherm constant (L/mg)
2.10.2 Freudlich isotherm

Freundlich isotherms are regularly used to describe the adsorption attributes of the heterogeneous surface (Hutson and Yang, 2000). The test information is regularly fitted in the experimental equations 2.11 proposed by Freundlich;

\[ q_e = K_F C_e^n \]  \hspace{1cm} 2.11

The linearized freudlich equation is presented as, in equation 2.12;

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  \hspace{1cm} 2.12

Where;

- \( K_F \) = Freundlich isotherm constant (mg/g)

- \( n \) = adsorptions intensity;

- \( C_e \) = the equilibrium concentrations of adsorbate (mg/L)

- \( q_e \) = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)

Plot of \( \frac{C_e}{q_e} \) versus \( C_e \) derived from linearized Langmuir equations gives a linear graph where the reciprocal of slope is used in calculations of the adsorption capacity. The Freundlich isotherm is determined by plotting \( \log q_e \) against \( \log C_e \).
CHAPTER THREE

MATERIALS AND METHODS

3.1 Collections and pre-treatment of raw materials

3.1.1 Rice husks ash (RHA)

Rice husks were provided by Euros rice millers in Kirinyaga County, Mwea west district, Kenya. They were washed several times with distilled water to remove soil and dust, dried in an oven at 100 °C for 2 hrs then burnt in a furnace at 800 °C in the presence of air for 3hrs to obtain ash (Chen, 2008). The sample was allowed to cool, crushed and stored in laboratory for further use.

Plate 3.1: Picture of rice husk ash before grinding

3.1.2 Sugarcane bagasse ash (SBA)

Sugarcane bagasse was obtained from a juice making shop at Kahawa Wendani, Nairobi, Kenya. They were washed several times with tap water followed by distilled water to remove impurities, dried in an oven at 100°C for 2hrs and then heated in a furnace at
500°C for 30 minute to obtain ash (Gupta et al., 2014). The sample was allowed to cool and stored in laboratory for further use.

Plate 3.2: Picture of sugarcane bagasse ash

3.1.3 Hydrothermal process

The materials used for the hydrothermal reactions were rice husk ash (RHA) as source of silica, NH₄OH, HCl and sugarcane bagasse as carbon source. NH₄OH (28%), served as a source of NH₃ which would provide a reduction atmosphere in addition to carried out nitridation. HCl (1.0 M) was added into the SiO₂ to act as a mineralizer and break it up (Chen, 2008). The reactor bomb was made of SS-316 stainless steel whose cylindrical primary body was 80 mm in outer breadth, 55 mm in inner width and 95 mm in length. The spread has inward screw strings and the primary body has external screw strings, so that could screw tight. The top screw front of the primary body was 80 mm in outside distance across, 43 mm in inward breadth, and 43mm in height. The viable warming area
of the radiator was one-third from the base of the chamber, and the upper area of the barrel was normally cooled.

3.1.4 Synthesis of silicon nitrides; SNA, SNB, SNC and SND

Approximately 25 grams of rice husk ash were soaked in HCl (1.0 M) for 3 hours, it was filtered and transferred to a bomb calorimetre, 5 grams of sugarcane bagasse ash and 150 mL of 28% ammonium hydroxide (NH₄OH) were added to the mixture. Teflon was wrapped around the threads before the bomb was tightly closed. The bomb calorimetre was heated at 100°C in thermostat-controlled furnace for 24hrs. The content was allowed to cool and then the resulting residue filtered using whatman No 1. Filter paper. The solid residue of silicon nitride was labeled SNA, the procedure was repeated at 150, 200, 300°C to give SNB, SNC and SND. SNB and SNC were washed with distilled water and dried to account weight.

3.2 Chemicals and reagents

All the chemicals used were of analytical grade. The chemicals were purchased from Sigma Aldrich (Germany).

3.2.1 Preparation of standard solutions

Fluoride ions stock standard solution of 1000 mg/L was obtained by dissolving 2.210 g of anhydrous sodium fluoride (Merck) and diluted to 1 litre in 1000 mL volumetric flask using distilled water. A working solution of 100 mg/L was obtained from the stock by
placing 10 mL of the stock solution in a 100 mL volumetric flask and making it to the mark using distilled water. Working fluoride ions standard solution of 2, 4, 6, 8 and 10 mg/L were prepared by adding 2, 4, 6, 8 and 10 mL of the working solutions into a 100 mL volumetric flask and diluting it to the mark using distilled water.

3.2.2. Fluoride buffer solutions

Ionic strength adjustment buffer (TISAB) solutions were made by adding 57 mL glacial acetic acid, 45 g sodium chloride and 4 g CDTA (1, 2-diamino cyclohexan N,N,N,N-tetra acetic acid) in 500 mL distilled water in a 1000 mL beaker and the mixture mixed to dissolve. The pH was adjusted to 5.5 by adding drops of 6N NaOH. The contents in the beaker were transferred into a 1 litre volumetric flask and filled up to the mark with distilled water.

3.3 Apparatus and instruments

The XRD- diffractograms were recorded using a Model D2 Phaser, Bruker AXS, Germany. XRF spectra were recorded using XRF 200 compact, while IR spectra were recorded using FTIR-8400 Spectrophotometre. Fluoride ions were determined using Fluoride ions selective electrode (ISE). Batch experiments were conducted, shaking at constant speeds using an Electric shaker (DKZ-1 NO.1007827). Other equipment used include the electric weighing balance (ATX224 Shimadzu), oven WTC binder (W×D×H=63.5×63×61.5cm), furnace (heat treatment kiln LNT, W×D×H=250×200×500cm), bomb calorimetre, magnetic stirrer and pH metre.
3.3.1 Characterizations of silicon nitride

3.3.1.1 X-ray diffractometry
The sample was prepared using the Millipore Filter Method-11 by using vacuum filter equipment (Schäfer et al., 2005). This was analyzed using XRD (D2 Phaser Model-Bruker) and Cu Kα radiation at 40 kV and 40 mA with a graphite monochromator ($\lambda=1.5418$ Å) at a scanning speed of $3^\circ 2\theta$/min within diffractions angle ranging from 5 to $65^\circ$. Diffrac-plus software was used to interpret the patterns. The intensity of the diffractions of a sample under investigations was continuously recorded as the sample and detector rotated through their respective angles. This guarantees high top/foundation proportions, low affectability to test thickness varieties and decent checking insights. The most grounded crests stayed inside the linearity scope of the counter and the beam stayed inside arrangement for the least $2\theta$ edge diffractions, from which the analysis was done. In addition, a calibration curve was obtained for the subjective estimations of free silicon in silicon nitride over the extent 0 to 0.3% by weight of Si.

3.3.1.2 Fourier transform infrared (FTIR)
All spectra were recorded on spectroscopy spectrophotometre on KBr pallets in the range $4000 - 400$ cm$^{-1}$. The pellets prepared by mixing 1 mg of the sample with 25 mg KBr, ground to fine powder and pressed under vacuum to a pellet. The pellet was examined using FTIR spectrophotometer (FTIR-8400) in the range $4000$ cm$^{-1}$ - $400$ cm$^{-1}$ as reported (Naja et al., 2005).
3.3.2 Electric shaker

Constant shaker (DKZ-1 NO.1007827) was used in shaking the samples at the required speed, it has a water bath which was used for temperature regulation.

3.3.3 Fluoride ion selective electrode (ISE)

The concentration of fluoride ion was determined using a calibrated Fluoride ISE Combined (Sentek, 48030/0001). Using manual instructions of optimum pH range: pH 4 to pH 8, temperature range: 0 to 80 °C and preconditioning time: 5 minutes were maintained (Skoog, 2004). The prescribed total ionic strength adjustment buffer (TISAB) was arranged and blended with sample solutions in the volume proportions of 1:1 to guarantee that every single measured solution had the same ionic quality and maintain a strategic distance from blunders because of contrasts between the deliberate movement and the real concentration. A steady agitation was kept up in order to permit a new supply of ions to be presented to the detecting bit of the ISE. Attractive stirrers can create adequate warmth to change the arrangement temperature. To balance this impact, a bit of Styrofoam sheet was placed between the stirrer and the measuring glass to go about as a protecting material. The cathode tip was washed and tenderly touched dry with a low-build up lab tissue between estimations utilizing refined water to guarantee exact readings.

3.3.4 pH metre

All pH estimations were performed using an adjusted Jenway 3505 pH-meter furnished with a standard calomel cathode (SCE). Buffer tablets for pH 4, 7 and 9 were each
dissolved up independently, in 100 cm$^3$ of distilled-deionized water in a measuring cylinder and used to calibrate the pH meter. The pH electrode was conditioned with saturated potassium chloride solutions over night to wet the membrane and improve its sensitivity. The pH meter was calibrated daily before any pH measurements were carried out in the laboratory (Vogel, 1978).

3.4 Batch adsorption experiments

All measurements were done in triplicate and averages used for the respective parameters; volume of fluoride ions solutions used for all experiments was 100 cm$^3$.

3.4.1 Optimization of temperature

This was determined by exposing 0.1 g of silicon nitride to 100 mL of initial fluoride ions concentrations of 2 mg/L at pH 2 for SNA, SNB, SNC and 6 mg/L at pH 5 for SND. The experiments were carried out at temperatures 20, 40, 50, 60 and 80°C. The fluoride solutions were agitated for 100 minutes, shaking speed of 120 rpm, after which the residue was filtered off using whatman No 1. filter paper. The residual fluoride ion concentration was determined using the fluoride ISE.

3.4.2 Optimization of pH

The effect of pH was investigated by varying it from pH 2 to 12. 0.1 M nitric acid or 0.1 M sodium hydroxide were used drop wise for adjustment of pH until the desired pH of 2, 5, 7, 9 and 12 were obtained. A mass of 0.1 g silicon nitride was weighed accurately and
added to 100 mL sample solutions containing 6 mg/L of fluoride ions. The contents were agitated for 100 minutes, shaking speed of 120 rpm while maintaining the temperature at 25°C. Thereafter, each sample was filtered using whatman No 1. filter paper, The residual fluoride ion concentration was determined using the fluoride ISE. The experiments were done and the average values used to calculate the optimum pH value.

3.4.3 Optimization of initial ion concentration

The initial fluoride ion concentration was varied from 2 - 10 mg/L at ideal temperature of 25°C and pH of 6. The analyses were done by utilizing 0.1 g of SNA, SNB, SNC and SND in 100 mL at shaking speed of 120 rpm. Samples were then filtered after 100 minutes and the filtrate were tested for the remaining fluoride ions using a fluoride ISE. The average values were used to calculate the amount and percentage of fluoride ions adsorbed from each initial concentration. The optimum value was obtained by taking the highest percentage amount of fluoride ions adsorbed per unit mass of the adsorbent.

The amount adsorbed at equilibrium, $q_e$ (mg/g), was calculated by equation 3.1;

$$q_e = \left( \frac{C_0 - C_e}{W} \right) V$$  \hspace{1cm} 3.1

Where $C_0$ and $C_e$ (mg/L) are the concentrations of respective metal ions at the initial and equilibrium conditions respectively. $V$ is the volume of the solutions (L) and $W$ is the mass of dry adsorbent used (g).
3.4.4 Optimization of sorbent dose

The sorbent dose of SNA, SNB, SNC, SND was varied from 0.1 g, 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g per 100 mL, using initial fluoride ions concentrations of 2 mg/L at pH 2 for SNA, SNB, SNC and 6 mg/L at pH 5 for SND. The experiment was carried out at a temperature of 25°C, shaking speed of 120 rpm and contact time of 100 minutes after which the samples were removed from the water bath and filtered the residue using whatman No 1. filter paper. The residual fluoride ion concentration was determined using the fluoride ISE.

3.4.5 Optimization of contact time

This was determined by varying the contact time from 20, 40, 60, 80 and 100 minutes, using 0.1 g of silicon nitride which was added to each bottle in initial fluoride ions concentrations of 6 mg/L at pH 5 for SND and 2 mg/L at pH 2 for SNA, SNB, SNC. The experiment was carried at a temperature of 25°C, the bottles were stirred on a shaker at 120 rpm, after which the samples were removed from the water bath and filtered the residue using whatman No 1. filter paper. The residual fluoride ion concentration was determined using the fluoride ISE.

3.4.6 Optimization of shaking speed

This was determined using an adsorbent dose of 0.1g of initial fluoride ions concentrations of 6 mg/L at pH 5 for SND and 2 mg/L at pH 2 for SNA, SNB, SNC. The experiment was carried out at a temperature of 25°C, and contact time of 100 minutes. The shaking speed interval was varied from 120, 240, 360, 480 and 600 rpm, after which
the samples were removed from the water bath and filtered using whatman No 1 filter paper. The residual fluoride ion concentration was determined using the fluoride ISE.

### 3.5 Data analysis

Data was fitted into Freundlich and Langmuir isotherms and were used to determine adsorptions capacities of the silicon nitride synthesized from rice husk ash and sugarcane bagasse at different temperature. The results are presented in chapter four.
CHAPTER FOUR

RESULTS AND DISCUSSIONS

Silicon nitride was prepared by hydrothermal method at four different temperatures and labeled SNA, SNB, SNC, SND. These were characterized by various spectroscopic/diffractions methods and the results are presented and discussed in the subsection that follows. They were also subjected to Fourier transform infrared spectroscopy (FTIR) for functional group determinations. The characterized silicon nitride samples were used in batch experiment to determine their adsorption capacity and efficiency under different conditions of temperature, pH, adsorbent dosage, contact time, initial ions concentration and shaking speed. The results and discussions are presented in this chapter.

4.1 Elemental analysis

The elemental composition of the SNA, SNB, SNC and SND were determined using the X-ray fluorescence (XRF) technique as the oxide and the results are shown in table 4.1.

Table 4.1: Percentage chemical composition of silicon nitrides SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>Nitride</th>
<th>SiO₂</th>
<th>Cl</th>
<th>Al₂O₃</th>
<th>P₂O₅</th>
<th>CaO</th>
<th>K₂O</th>
<th>Fe₂O₃</th>
<th>CuO</th>
<th>NiO</th>
<th>Cr₂O₃</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNA</td>
<td>90.10</td>
<td>3.48</td>
<td>1.67</td>
<td>0.56</td>
<td>0.85</td>
<td>0.40</td>
<td>1.82</td>
<td>0.29</td>
<td>0.29</td>
<td>0.19</td>
<td>0.00</td>
</tr>
<tr>
<td>SNB</td>
<td>94.19</td>
<td>1.73</td>
<td>1.19</td>
<td>0.20</td>
<td>0.33</td>
<td>0.37</td>
<td>0.55</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>1.161</td>
</tr>
<tr>
<td>SNC</td>
<td>93.47</td>
<td>1.79</td>
<td>1.41</td>
<td>0.19</td>
<td>0.43</td>
<td>0.34</td>
<td>0.92</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>1.08</td>
</tr>
<tr>
<td>SND</td>
<td>90.69</td>
<td>4.51</td>
<td>0.97</td>
<td>0.33</td>
<td>0.55</td>
<td>0.43</td>
<td>0.93</td>
<td>ND</td>
<td>0.11</td>
<td>0.12</td>
<td>0.98</td>
</tr>
</tbody>
</table>
As shown in the table, the percentages of Cl were found to be higher in SND and SNA at 4.51 and 3.48 than in SNB and SNC at 1.73 and 1.79 respectively. This is attributed to the pretreatment of the products after synthesis. Whereas, all the products (SNA, SNB, SNC and SND) were leached with 1.0 M HCl, SNB and SNC were washed with distilled water after leaching; the SNA and SND were not. Leaching with HCl leads to material having high level of chloride while distilled water removes the surface chlorides as observed by Baris (2014). Consequently, XRF analysis showed that SNB and SNC had higher silica percentage at 94.19 and 93.47 compared to SND and SNA at 90.69 and 90.10 % respectively.

It is clear that the major component of the silicon nitride is Si. However, other elements seen include Aluminium, alkali metals, alkaline earth metals, iron and phosphorus, and they are all in small amounts.

4.2 X-ray diffractions

Characterizations and phase analysis of adsorbent material was done using x-ray diffractions. The diffractogram of SNA is presented by figure 4.1.
Figure 4.1: XRD pattern of adsorbent SNA

The phase matches identified for SNA adsorbent material correspond to α-silicon nitride and β-silicon nitride. The degree of crystallinity was determined using the procedure reported by Sanjeeva (2004). The material had a degree of crystallinity of 64.28 wt% and 35.27 wt% amorphous. These values for the percentage crystallinity indicate semi crystallinity (Treacy and Higgins, 2007). The material contained a higher percentage of α-phase (64.6%) of silicon nitride as compared to the β-phase (27.8%) as implied by figure 4.1.

Although SNA was synthesized hydrothermally at 100°C for 24 hours, a relatively lower temperature when compared to others in literature, the result agrees with the findings of Chen (2008) who reported that the peaks of SiC and Si₃N₄ get sharper and stronger as temperature increases. Chen’s work found out that the percentage of crystallinity reduced
with increase in the duration of synthesis while lattice twisting increased as the reaction temperature was increased. The Si-bond absorbed more nitrogen under NH₄OH condition which lead to the broadening of the peak. Moreover, it was observed that increase in reaction temperature of 300°C made all of the peaks sharper and broader as compared to those of the product synthesized at 250°C. Therefore, we can conclude that increase in temperature and duration helps in the formation of Si₃N₄ and SiC.

Baris (2014) reported that the crystallinity of the silicon nitride formed after 24 hrs was higher than that formed after 6 hrs as indicated by their XRD patterns. Furthermore, the weight percentage of silicon nitride in the product was found to increase with increase in reaction duration. The weight percentage of silicon nitride increased from 85 after 3hrs reaction duration to around 95% wt after 24hrs.

4.3 Characterization of synthesized silicon nitride by FTIR spectroscopy

Figures 4.2, 4.3, 4.4 and 4.5 show FTIR spectra of silicon nitrides SNA, SNB, SNC and SND, respectively synthesized at various temperatures of 100, 150, 200, 300°C.
Figure 4.2: FTIR spectrum of silicon nitride, SNA synthesized at 100°C

The FTIR spectra of SNA which was synthesized at 100°C shows absorption band at 411.8, 470.6, 610.4, 671.2, 702.0, 803.3, 920.9, 1073.1 and 1400.2 cm\(^{-1}\). The absorption band at 470.6 cm\(^{-1}\) is attributed to Si-N (stretching), at this wave-number, there is overlap of Si-O with Si-N, implying amorphous phase (Chen, 2008). A weak band at 671.2 cm\(^{-1}\) which is characteristic of a silicon nitride Si-N-Si stretching vibrations was observed (Frajkorova et al., 2001). The bands at 803.3 cm\(^{-1}\) and 1107.1 cm\(^{-1}\) are attributed to the Si-C and Si-O-Si, respectively.
The FTIR spectra of SNB, SNC and SND are similar to that of SNA. However, figure 4.3 shows a clearer overlap of Si-O and Si-N vibrations at 470.6 cm\(^{-1}\), due to the overlap, can assume that it may be present in amorphous phase and covered by Si-O bonding (Chen, 2008).

Figure 4.3: FTIR spectrum of silicon nitride, SNB synthesized at 150°C
The FTIR spectrum of SNC which was synthesized at 200°C is shown in figure 4.4. Remarkably, the band at 574.7 cm\(^{-1}\) similar to that reported by Takase and Tani (1986) as originating from Si-N vibrations attributed to \(\alpha\)-silicon nitride. The absorption band at 1110.0 cm\(^{-1}\) is attributed to Si-O-Si bonding (Chen, 2008) while the characteristics stretching vibration band of silicon nitride were observed at 669.3 cm\(^{-1}\) (Frajkorova et al., 2001). The broad peak at 791 cm\(^{-1}\) show an overlap of Si-C in addition to Si-O and Si-N vibration observed at 464.6 cm\(^{-1}\).
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Figure 4.5: FTIR spectrum of synthesized silicon nitride at 300°C

The spectrum of SND, synthesized at 300°C is shown in figure 4.5. As observed from FTIR spectra of the four silicon nitride materials, the spectral peaks become sharper as synthesis temperature was increased from 100 to 300°C as reported by Chen (2008). Further bands at 477.3 cm\(^{-1}\) and 791.7 cm\(^{-1}\) related to overlapping (Si-O and Si-N) and (Si-N and Si-C) vibrations (Rudolphi et al., 2007), become more resolved. Therefore, the FTIR confirms the synthesis of silicon nitride.

4.4 Adsorption of fluoride ions by silicon nitride

4.4.1 Effect of pH

The effect of pH on removal of fluoride was studied in triplicate by varying pH from 2.0 to 12.0 using adsorbent dose of 0.1g/100mL. The temperature of the solution was maintained at 25°C, shaking speed at 120 rpm, contact time at 100 minutes and fluoride
ion concentrations at 6 mg/L. The results are illustrated in Figure 4.6. The percentage removal of fluoride ion by SNA ranged from about 56.5 to 50.0%, while that of SNB ranged from 59.0 to 54.0%, between pH 2 and 12. The percentage removal by SNC ranged from about 56.0% to 53.0% while that of SND varied from 63.5 to 61.0% between pH 2 and 12. This shows that pH has little effect on the percentage removal of fluoride ions from contaminated water. It is however clear that the optimum pH values for batch adsorption defloridation experiments were 2 for SNA, SNB, SNC and 5 for SND. These were used for all the batch experiments described in the thesis.

![Graph showing the effect of pH on the removal of fluoride ions using SNA, SNB, SNC and SND.](image)

**Figure 4.6: Effect of pH on the removal fluoride ions using SNA, SNB, SNC and SND**

There is increase in the percentage amount of fluoride ions adsorbed from 63.5% to 64.6% when the pH was varied from 2 to 5 for SND as shown in graph (Figure 4.6). As the pH was increased from 5 to 12, the amount of fluoride ions adsorbed by the SND decreased from 64.6% to 61.8% which is statistically significant as shown in appendix 2.
The minimum amount of fluoride ions adsorbed occurred at pH of 12. Because of higher H\textsuperscript{+} ions concentration at lower pH, the negative charges on the adsorbent surface get neutralized. This in turn reduces the hindrance to diffusion of negatively charged fluoride ions and gives rise to the more active surface for adsorption. The same trend was also observed in the study done by Basu et al. (2012) on the Batch adsorption of fluoride ions onto microwave assisted activated carbon derived from Acacia auriculiformis scrap wood, as pH values increased from 2 to 4.4. It may be due to the fact that initially at lower pH, the formation of weak hydrofluoric acid took place which retards the rate of fluoride adsorption.

For SNA, SNB and SNC, it was observed that as the pH increases, there was decrease in the amount adsorbed as shown in the Figure 4.6. The highest adsorption values were observed at pH 2, where the overall surface charged on the biosorbent may be positive. This empowered the binding of negative charged fluoride ions. At lower pH values, the surface of the adsorbent ended up being positively charged and this enhanced sorption of fluoride ions, likely by the anionic exchange sorption. At lower pH, because of the protonation, impact of surface functional groups, such as, thiol, carboxyl, and amino, confers positive charge at surface (Ilhami et al., 2005). Relative sorption inhibitions observed at basic pH range is attributed to the increase of hydroxyl ions leading to formation of aqua-complexes; thereby, retarding the sorption (Mohan and Karthikeyan, 1997).
4.4.2 Effect of adsorbent dose

The impact of dose on fluoride ions adsorption was investigated using adsorbent materials SNA, SNB, SNC and SND at different adsorbent dose values ranging from 0.2 to 1.0 g. Temperature was maintained at 25°C, shaking speed at 120 rpm, pH at 2 for SNA, SNB, SNC and 5 for SND, contact time was 100 minutes, and fluoride ion concentrations 6 mg/L for SND and 2 mg/L for SNA, SNB, SNC. The results are displayed in figure 4.7.

![Figure 4.7: Effect of adsorbent dose on removal fluoride ions using SNA, SNB, SNC and SND](image)

The percentage removal of fluoride ions by SNA and SND gradually increased from 74.8 to 88.2% and 69.0 to 80.0% respectively, at dose of 0.2 to 1.0 g which is not significant, as shown in appendix 3. Percentage fluoride ions removal by SNB ranged from 77.8 to 81.2% at dose of 0.2 to 0.6 g respectively and optimized at adsorbent dose of 1.0 g which achieved 81.75% removal. At 0.2 to 0.6 g, removal percentage by SNC is 71.2 to 75.2%
which is quite significant and attained optimum at dose of 1.0 g with 80.2% removal.

As shown in (Figure 4.7), percent removal increased to an optimum value with increase in sorbent dosage. It has been observed that up to certain level of higher doses of adsorbents, it resulted into higher removal of fluoride. This is a direct result of higher accessibility of surface and pore volume at higher measurement of the adsorbent. The increasing dosage increases surface range and active destination accessible for adsorption of fluoride ions.

This increment in adsorption with dosage can be ascribed to expanded surface zone and the accessibility of more binding destination for adsorption (Vasudevan and Lakshmi, 2011). This likewise correlate to investigation of Gupta et al. (2010) on batch and column operation for the removal of fluoride ions from aqueous solutions using fly bottom ash, that fluoride ions uptake was low at low bottom ash dose and expanded with dosage. This is due to a low dose, all types of sites are entirely exposed and the adsorption on the surface are saturated faster, showing a higher qe value. However, at a higher adsorbent measurement, the accessibility of higher energy sites diminishes with a bigger portions of lower energy destinations occupied, bringing about a lower qe value (Gupta et al., 2010).

However, it can be seen from SNA and SND that there was no significant difference in rate removal of fluoride, as shown in appendix 3. It was because of the overlapping of active destinations at higher measurements, consequently decreasing of the net surface
regions (Killedar and Bhargava, 1993). This compares to Alagumuthu et al. (2010), discoveries which reported that expanding the adsorbent measurement relatively build the rate expulsions of fluoride ions until an ideal quality. A dispersions coefficient $K_D$ mirrors the coupling capacity of the surface for a component. The $K_D$ estimations of a framework for the most part relies on upon pH and sort of surface.

### 4.4.3 Effect of contact time

The contact time was varied from 20, 40, 60, 80 and 100 minutes. Temperature was maintained at 25°C, shaking speed at 120 rpm, adsorbent dose of 0.1 g, pH at 2 for SNA, SNB, SNC and 5 for SND, and fluoride ions concentrations 6 mg/L for SND and 2 mg/L for SNA, SNB, SNC. This is presented in figure 4.8

![Figure 4.8: Effect of contact time on the removal of fluoride ions using SNA, SNB, SNC and SND](image)

**Figure 4.8: Effect of contact time on the removal of fluoride ions using SNA, SNB, SNC and SND**
The percentage removal of fluoride by SNA and SNB ranges from 75.6 to 82.0% and 76.0 to 82.0% respectively, while removal by SNC and SND range from 80.2 to 82.0% and 60.0 to 73.0% between 20 to 90 minutes respectively. This shows that beyond 20 minutes, most Fluoride ions have been adsorbed and contact time has little effect on percentage removal of fluoride ions in contaminated water, because the increase was not statistically significant, as shown in appendix 4.

The percentage removal also increased as contact time increased. However, it gradually approached an almost maintained value, revealing attainment of equilibrium. Overall removal of fluoride ions for SND, occurred in three separate stages as showed in Figure 4.8. The initial stage showed the harmony stage in which the sorption uptake was generally little. The second stage assigned the moderate uptake of fluoride ions that demonstrated the utilization of every single active site over the adsorbent surface and fulfilment of saturation or equilibrium stage. The third peak showed the high sorption uptake of the fluoride ions on to adsorbent. Comparable result trend were reported by Ramanaiah et al. (2007) who studied fluoride removal on biomass of Spirogyra sp. The initial quick sorption may be because of functional groups, and active surface destinations on adsorbent surface. Presence of such surface and functional groups on biomass based adsorbent and initial quick sorption was accounted for by different scientists (Mohan and Karthikeyan, 1997).

Increment in adsorption with contact time can be attributed to increase the surface region and the accessibility of all the more binding destinations for adsorption. It can likewise be
because of the dispersions of fluoride ions into the surface pores of the adsorbent. In SNA, after sometime, the increase was less due to the migration of fluoride ions from upper adsorbent surface to inner pores (Awan et al., 2012). As time increases, there is less and less number of adsorption sites remaining hence reductions in increase in rate of adsorption. This could have been attributed by the difference in pore sizes of the adsorbents since the larger the pore sizes, the larger the adsorption capacity (Mangun et al., 1998). SNC shows that there was equilibrium from 20 to 80 minutes, and this can be attributed to decrease in binding sites as the contact time increases.

**4.4.4 Effect of temperature**

Temperature influences the adsorption rate by adjusting the molecular connections and the solvency of the adsorbate (Singh et al., 2001). Adsorption studies were done at different temperatures (20, 40, 50, 60 and 80 ºC) using adsorbent material SNA, SNB, SNC, SND of 0.1 g, shaking speed of 120 rpm, contact time of 100 minute, pH 5 for SND, 2 for SNA, SNB, SNC, initial fluoride ions concentrations of 6 mg/L for SND, 2 mg/L for SNA, SNB, SNC. The result is illustrated in figure 4.9.
Figure 4.9: Effect of temperature on removal of fluoride ions using SNA, SNB, SNC and SND

It was observed that Adsorption of fluoride ions decreased from 62.0% to 54.0% when the temperature was increased from 20°C to 80°C for SND, percent removal when SNA was used with varying temperature decreased from 79.0% to 66.5% at temperature of 20 °C to 80 °C, when SNB was used the adsorption rate decreased from 81.2% to 76.8% at temperature of 20°C to 80°C, while using SNC, the adsorption rate decreased from 80.8% to 61.0% at temperature of 20°C 80 °C, all the decrease were statistically significant as shown in appendix 6, respectively.

These results indicate that high temperatures work against de-fluoridations by silicon nitride. This is on the grounds that with increasing temperature, the attractive force between adsorbent surface and fluoride ions are weakened and the sorption diminishes. Thus, at 20°C highest amount of fluoride has been removed. This outcomes are in
concurrence with Zhao et al. (2010), examinations on fluoride removal from aqueous solutions using synthesized Fe$_3$O$_4$-Al(OH)$_3$ attractive nanoparticles. The adsorption capacity decreased with temperature. At high temperature, the thickness of the limit layer decreases because of the high propensity of the fluoride ions to escape from the adsorbent surface to the arrangement stage which results in a lessening in adsorption as temperature increases (Aksu and Kutsal, 1991). Increase in temperature increases the rate of diffusion of the sorbate ions towards the sorbent surface and at the same time, some sorbate ions acquire enough thermal energy and diffuse away from the monolayer surface.

This implies that the rate of desorption was higher than the rate of adsorption, which means that adsorption is an exothermic reaction (Ali, 2011). The reduction in the measure of fluoride ions adsorbed with temperature shows an exothermic nature of the process. It is clear that the temperature of the adsorption medium could be important for energy dependent mechanisms in fluoride ions binding process.

4.4.5 Effect on shaking speed

The agitation of fluoride solutions was carried out in an electric shaker at ambient temperature. The agitation speed varied from 120, 240, 360, 480 and 600 rpm. Temperature was maintained at 25°C, contact time of 100 minutes, adsorbent dose of 0.1 g, pH at 2 for SNA, SNB, SNC and 5 for SND, and fluoride ions concentration 6 mg/L for SND and 2 mg/L for SNA, SNB and SNC. The result is presented in figure 4.10.
Figure 4.10: Effect of shaking speed on removal of fluoride ions using SNA, SNB, SNC and SND.

Fluoride uptake increased with the increase in shaking rate. Percentage removal of fluoride ions increases significantly from 61.0% at shaking speed of 120 rpm to 62.0, 63.0 and 64.0% at a shaking speed of 240, 360 and 480 rpm for SND. Percentage removal of fluoride ions increased significantly from 76.5% at shaking speed of 120 rpm to 78.0, 79.5 and 79.8% at a shaking speed of 240, 360 and 480 rpm then attained maximum percent removal at 80.5% at 600 rpm when adsorbent SNA was used.

For SNB, 79.2% was recorded at shaking speed of 120 rpm which increased to 79.8, 80.5, 80.5 and 81.5% at shaking speed of 240, 360, 480 and 600 rpm. Furthermore, when SNC was used, percentage removal of fluoride ions changes from 78.75% at shaking speed of 120 rpm to 78.8, 81.0, 81.5 and 81.5% at shaking speed of 240, 360, 480 and 600 rpm respectively. For SNB and SNC, the increase in percentage removal did not vary
significantly, as indicated in appendix 5. The optimum shaking speed for the removal of fluoride ions using all the adsorbents was 600 rpm.

These results can be connected with the way that increase in the unsettling speed enhances the diffusion of fluoride ions towards the surface of the adsorbent, and in this manner, proper contact is produced between fluoride ions in solutions and the binding destinations. This advances exchange of sorbate ions to the sorbent destinations. Higher uptake of fluoride ions could be conceivable at higher rate of shaking as it will guarantee that all adsorption destination are made promptly accessible for fluoride ions uptake. This pattern is in concurrence with results reported by Bernard et al. (2013).

While increasing the shaking speed, the dissemination rate of ions from the mass fluid to the fluid limit layer encompassing sorbent ions gets to be higher in view of an upgrade of turbulence and decrease of the thickness of the fluid limit layer (Nomanbhay and Palanisamy, 2005). Great dissemination of ions toward the sorbent particles is additionally guaranteed. Increasing the agitation rate build the outside film mass exchange and coefficient consequently the rate of uptake (Low and Lee, 1997). This is because of decrease of the film limit layer encompassing the sorbent particles.

Awan et al. (2012) also observed that at lower rpm, the removal capacity was low but as the rpm increased, the fluoride removal also increased, and this might be due to the better contact between adsorbate and adsorbent at high rpm. Increase in kinetic energy increases
the rate of diffusions of fluoride ions hence more fluoride ions reach the adsorbent surface thereby increasing the rate of both physisorption and chemisorption (Shafqat et al., 2008). If shaking speed is low, silicon nitride accumulates instead of spreading in the sample and various active sites are buried under the outer layer reducing the rate of adsorption. This indicates that shaking speed should be sufficient to ensure that all the surface binding sites are available for fluoride ions uptake.

4.4.6 Effects of initial ions concentration

The experiments were carried out using 100 mL of analyte solutions with concentrations varying from 2 to 10 mg/L at pH 6. For adsorbent material SNA, SNB, SNC and SND an amount of 0.1 g/100 mL of adsorbent was used for each adsorption experiment, shaking speed of 120 rpm, temperature of 25°C and contact time 100 minutes. The results are shown in figure 4.11.

![Figure 4.11: Effect of initial concentrations on removal of fluoride ions using SNA, SNB, SNC and SND.](image)

Figure 4.11: Effect of initial concentrations on removal of fluoride ions using SNA, SNB, SNC and SND.
As the initial concentrations increased from 2 mg/L to 6 mg/L, there was an increase in the percentage quantity of fluoride ions adsorbed by the adsorbent from 62.5% to 65.0%, increase in initial ions concentration above 6 mg/L was accompanied by a decrease in percentage de-fluoridations by using SND. The percent removal of fluoride was about 75.0% at initial concentrations of 2 mg/L and then reduced to 54.0% at 10 mg/L when using SNA. For SNB, the percentage removal dropped from about 72.0% for initial concentrations of 2 mg/L to 54.0% at 10 mg/L, while when using SNC, the percentage removal of fluoride decreased from about 66.0% for initial concentrations of 2 mg/L to 56.8% at 10 mg/L.

The increase in percentage removal by using SND from 62.5 to 65.0% is probably due to larger surface area of the SND being available at beginning for the adsorption of fluoride ions. The decrease in percentage removal above 6 mg/L is on account of the surface adsorption destinations get to be depleted; the uptake rate was controlled by the rate at which the adsorbate was transported from the outside to the inside sites of the adsorbent particles.

The highest adsorption rate of fluoride particles happened at a fundamental molecule gathering of 6 mg/L. At this underlying fluoride particle fixation, 65.0% of the underlying grouping of fluoride particles was adsorbed. Introductory particle convergence of 6 mg/L was recorded as the ideal focus and utilized as a part of all fluoride adsorptions tests where different parameters were varied for SND. There was an
expansion in adsorption because of an increment in the measure of the fluoride particles bound on the surface of the adsorbent. Lv et al. (2006) acquired a comparative pattern in their study on fluoride particle expulsions with MgAl-CO$_3$. As per Malakootian et al. (2011), expulsions of fluoride particles from fluid arrangement by pumice demonstrated an expansion in adsorbed rate as beginning fluoride fixations was expanded because of a bring up in the main impetus of the focus slope.

When using SNA, SNB and SNC, the percentage removal decreases as the initial concentration increases, because the adsorbent materials get depleted forcefully with the expansion in initial fluoride concentration. This was because of the way that for an altered adsorbent measurement, the aggregate accessible adsorption sites were constrained, which got to be soaked at a large concentration. Comparative pattern has been accounted for fluoride removal by utilizing charcoal of a Neem (Chakrabarty and Sarma, 2012). The contrast between the mean rate removal for SNA, SNB, SNC and SND varied essentially as the concentration of fluoride increased. This could be due to the distinction in pore sizes and level of crystallinity of the adsorbents. Adsorbent with bigger pore sizes are preferred over those with smaller pore sizes. The higher the level of crystallinity, the better the spreading of pores, makes them more accessible for adsorption. Several researchers have found that there is a decline of removal of fluoride ions with increase of initial concentration (Baral et al., 2008).
4.5 Adsorption isotherms

The (Freundlich and Hatfield, 1926) and (Langmuir, 1918) models are the most utilized models in adsorption studies. Equilibrium data acquired were fitted into Langmuir and Freundlich isotherms models. Thermodynamic information of fluoride adsorptions using SNA, SNB, SNC and SND are presented in table 4.2.

Table 4.2: Equilibrium data for fluoride adsorption using SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>Ions</th>
<th>Adsorbents</th>
<th>Qmax (mg/g)</th>
<th>b(dmg3/g)</th>
<th>R^2</th>
<th>1/n</th>
<th>kf (mg/g)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>SNA</td>
<td>7.8554</td>
<td>0.4829</td>
<td>0.9888</td>
<td>0.5447</td>
<td>2.4468</td>
<td>0.9531</td>
</tr>
<tr>
<td></td>
<td>SNB</td>
<td>8.9454</td>
<td>0.3450</td>
<td>0.9977</td>
<td>0.6189</td>
<td>2.2299</td>
<td>0.9737</td>
</tr>
<tr>
<td></td>
<td>SNC</td>
<td>13.9</td>
<td>0.1534</td>
<td>0.9992</td>
<td>0.7943</td>
<td>1.8213</td>
<td>0.9981</td>
</tr>
<tr>
<td></td>
<td>SND</td>
<td>49.75</td>
<td>0.0352</td>
<td>0.9792</td>
<td>0.8561</td>
<td>1.7697</td>
<td>0.9455</td>
</tr>
</tbody>
</table>

Qmax= adsorptions capacity of Langmuir, b= Langmuir equilibrium constant associated with energy of adsorptions, R^2=Correlations coefficient, 1/n = heterogeneity parameter and kf = adsorptions capacity of Freundlich.

The adsorptions data of fluoride ions on SNA, SNB, SNC and SND fitted best into Langmuir adsorption isotherm model based on the R^2 values of 0.9888, 0.9977, 0.9992 and 0.9792 respectively. This implies that the Langmuir adsorptions isotherm has higher values of R^2 hence it fits well to the experimental data obtained than the Freundlich adsorption isotherm, for fluoride ions. This indicates that the adsorption of fluoride ions on the SNA, SNB, SNC and SND are monolayer.

The Langmuir b values for SNA, SNB, SNC and SND were 0.4829, 0.3450, 0.1534 and 0.0352 indicating that the values decreased as the temperature of the hydrothermal synthesis increased. The value of b indicates the adsorption nature to be unfavourable if b > 1, linear if b =1, favourable if 0 < b < 1, and irreversible if b =0, therefore, the values
indicate that Langmuir isotherm is favourable. The adsorption capacities of SNA, SNB, SNC and SND were 7.9, 8.9, 13.9, 49.8 mg/g, this implies that the adsorption capacity increases as the temperature increases. The adsorption capacity values were higher than those of adsorbents reported in table 4.3. This suggests adsorbent SND is preferred adsorbent over the reported adsorbents. This is on the grounds that most adsorbents contain smaller scale pores and the adsorption procedure is influenced by surface properties, for example, surface regions and extremity. A large surface zone is best to provide huge adsorption capacity. The size of the miniaturized scale pores determined the accessibility of the sorbate molecule to the adsorption surface (Igwe and Abis, 2006).

Table 4.3: Comparison of monolayer adsorptions capacities of silicon nitrides (SNA, SNB, SNC and SND) with other adsorbents for fluoride.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Adsorbent</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride ions</td>
<td>Rice</td>
<td>0.019</td>
<td>Wahecd et al., 2009</td>
</tr>
<tr>
<td></td>
<td>Ground nut shell</td>
<td>2.32</td>
<td>Veeraputhiran et al., 2011</td>
</tr>
<tr>
<td></td>
<td><em>Cynodon Dactylon</em></td>
<td>4.617</td>
<td>Alugumuthu et al., 2010</td>
</tr>
<tr>
<td></td>
<td><em>Acacia auriculiformis</em></td>
<td>18.95</td>
<td>Basu et al., 2012</td>
</tr>
</tbody>
</table>

Regarding Freundlich isotherm, the slope 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, it becomes more heterogeneous if its value gets closer to zero. A value for 1/n below one indicates a normal Langmuir isotherm while 1/n above one is an indicative of cooperative adsorption and it also implies that the adsorption is favorable. 1/n Values of 0.5447, 0.8561, 0.7943 and 0.8561 were observed
for fluoride ions for SNA, SNB, SNC and SND respectively indicating a normal Langmuir fit.
CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The rice husks contained high amount silica with minute impurities. Silicon nitride was successfully synthesized from rice husks and sugarcane bagasse ashes at various temperatures of 100, 150, 200 and 300°C for 24 hrs.

Adsorbent SNA, SNB, SNC and SND are good adsorbents of fluoride ions, based on their percentage fluoride removal values registered at different initial ions concentration, pH, contact time, shaking speed, temperature and adsorbent dose varied.

SND was a better adsorbent than the other adsorbents, based on its adsorption capacity of fluoride ions attained on the adsorbent.

The present study shows that the SND can be employed as potentially effective adsorbents for removal of fluoride ions from contaminated water. The adsorption capacities of the synthesized adsorbents were found to be greatly dependent on the initial fluoride ions concentration, shaking speed, contact time, temperature of the solutions.

Silicon nitride powder may be particularly appropriate for the treatment of small quantities of drinking water containing fluoride ions and the data reported could be useful for the design batch or stir-tank flow reactor.
5.2 Recommendations

i. Adsorbent SNA, SNB, SNC and SND have shown good potential of adsorbing fluoride from synthetic waste water but further research need to be done to verify its effectiveness in removing these fluoride ions from industrial waste water. Related research also needs to be done to find out whether it is capable of adsorbing other anions and cations from wastewater.

ii. Other sources of silica such as rice straw, corn bobs and bagasse need to be investigated on effectiveness of producing silicon nitride.

iii. Studies need to be conducted on regenerations of silicon nitride adsorbent.

iv. Further studies on characterization of silicon nitride using Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), need to be carried out.
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Kurama H., and Kurama S. K. (2003). The Effect of Chemical Treatment on the Productions of Active Silica from Rice Husk. 18th International Mining Congress and Exhibitions of Turkey-IMCET.


Appendix 1: Effect of initial concentrations on mean percentage removal of fluoride using SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>Concentrations (mg/L)</th>
<th>Mean percentage removal for SNA Mean±SD</th>
<th>Mean percentage removal for SNB Mean±SD</th>
<th>Mean percentage removal for SNC Mean±SD</th>
<th>Mean percentage removal for SND Mean±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mg/L</td>
<td>0.50±0.10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.56±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.68±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.75±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>4 mg/L</td>
<td>1.07±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.25±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.49±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.43±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>6 mg/L</td>
<td>2.07±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.08±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.31±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.60±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>8 mg/L</td>
<td>3.54±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>3.45±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.31±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.52±0.10&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>10 mg/L</td>
<td>4.54±0.00&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.57±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.32±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.00±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Means that do not share a letter are significantly different.

Appendix 2: Effect of pH on mean percentage removal of fluoride using SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>pH</th>
<th>Mean percentage removal for SNA Mean±SD</th>
<th>Mean percentage removal for SNB Mean±SD</th>
<th>Mean percentage removal for SNC Mean±SD</th>
<th>Mean percentage removal for SND Mean±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.61±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.45±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.61±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.18±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>2.76±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.57±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.67±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.12±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>2.86±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.63±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.65±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.21±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>9</td>
<td>2.84±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.61±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.71±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.24±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>12</td>
<td>2.97±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.73±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.79±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.24±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Mean that do not share a letter are significantly different.
Appendix 3: Effect of Adsorbent dosage on percentage removal of fluoride using SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>Dose (g)</th>
<th>Mean percentage removal for SNA Mean±SD</th>
<th>Mean percentage removal for SNB Mean±SD</th>
<th>Mean percentage removal for SNC Mean±SD</th>
<th>Mean percentage removal for SND Mean±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 g</td>
<td>0.50±0.10&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.44±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.57±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.65±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.4 g</td>
<td>0.45±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.41±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.53±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.60±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.6 g</td>
<td>0.41±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.40±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.49±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.54±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>0.8 g</td>
<td>0.38±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.37±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.49±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.44±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>1.0 g</td>
<td>0.23±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.36±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.39±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.43±0.41&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Mean that do not share a letter are significant different

Appendix 4: Effect of contact time on percentage removal of fluoride using SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Mean percentage removal for SNA Mean±SD</th>
<th>Mean percentage removal for SNB Mean±SD</th>
<th>Mean percentage removal for SNC Mean±SD</th>
<th>Mean percentage removal for SND Mean±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min</td>
<td>0.48±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.48±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.39±0.01&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>2.36±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>40 min</td>
<td>0.42±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.41±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.38±0.01&lt;sup&gt;abc&lt;/sup&gt;</td>
<td>2.23±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>60 min</td>
<td>0.41±0.01&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>0.40±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.40±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.21±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>80 min</td>
<td>0.38±0.00&lt;sup&gt;cd&lt;/sup&gt;</td>
<td>0.39±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.37±0.01&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>2.21±0.25&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>100 min</td>
<td>0.36±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.35±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.36±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.62±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Mean that do not share same letter are significant different
Appendix 5: Effect of shaking speed on percentage removal of fluoride using adsorbent SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>Shaking Speed (rpm)</th>
<th>Mean percentage removal for SNA Mean±SD</th>
<th>Mean percentage removal for SNB Mean±SD</th>
<th>Mean percentage removal for SNC Mean±SD</th>
<th>Mean percentage removal for SND Mean±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 rpm</td>
<td>0.47±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.41±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.42±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.38±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>240 rpm</td>
<td>0.44±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.40±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.42±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.28±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>360 rpm</td>
<td>0.41±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.39±0.01&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>0.38±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.23±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>480 rpm</td>
<td>0.40±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.39±0.01&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>0.37±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.21±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>600 rpm</td>
<td>0.39±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.37±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.36±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.14±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Mean that do not share a letter are significant different.

Appendix 6: Effect of temperature on mean percentage removal of fluoride using adsorbent SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Mean percentage removal for SNA Mean±SD</th>
<th>Mean percentage removal for SNB Mean±SD</th>
<th>Mean percentage removal for SNC Mean±SD</th>
<th>Mean percentage removal for SND Mean±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>0.42±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.37±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.43±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.27±0.01&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>40°C</td>
<td>0.42±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.38±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.41±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.34±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>50°C</td>
<td>0.46±0.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.39±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.78±0.01&lt;sup&gt;bc&lt;/sup&gt;</td>
<td>2.44±0.00&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>60°C</td>
<td>0.49±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.45±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.39±0.01&lt;sup&gt;cd&lt;/sup&gt;</td>
<td>2.48±0.01&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>80°C</td>
<td>0.67±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.43±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.38±0.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.75±0.01&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Mean that do not share a letter are significant different.
### Appendix 7: Effect of pH on mean percentage of fluoride adsorbed using SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>pH</th>
<th>% fluoride ions adsorbed for SNA</th>
<th>% fluoride ions adsorbed for SNB</th>
<th>% fluoride ions adsorbed for SNC</th>
<th>% fluoride ions adsorbed for SND</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>56.50</td>
<td>59.00</td>
<td>56.00</td>
<td>63.50</td>
</tr>
<tr>
<td>5</td>
<td>54.00</td>
<td>57.00</td>
<td>55.00</td>
<td>64.60</td>
</tr>
<tr>
<td>7</td>
<td>52.00</td>
<td>56.00</td>
<td>55.80</td>
<td>63.10</td>
</tr>
<tr>
<td>9</td>
<td>52.00</td>
<td>56.00</td>
<td>54.00</td>
<td>62.60</td>
</tr>
<tr>
<td>12</td>
<td>50.00</td>
<td>54.00</td>
<td>53.00</td>
<td>61.80</td>
</tr>
</tbody>
</table>

### Appendix 8: Effect of adsorbent dose on mean percentage of fluoride adsorbed using SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>Adsorbents dose (g)</th>
<th>% fluoride ions adsorbed for SNA</th>
<th>% fluoride ions adsorbed for SNB</th>
<th>% fluoride ions adsorbed for SNC</th>
<th>% fluoride ions adsorbed for SND</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 g</td>
<td>74.75</td>
<td>77.75</td>
<td>71.25</td>
<td>72.00</td>
</tr>
<tr>
<td>0.4 g</td>
<td>77.50</td>
<td>79.25</td>
<td>73.50</td>
<td>73.00</td>
</tr>
<tr>
<td>0.6 g</td>
<td>79.25</td>
<td>81.25</td>
<td>75.25</td>
<td>74.00</td>
</tr>
<tr>
<td>0.8 g</td>
<td>80.75</td>
<td>81.25</td>
<td>75.50</td>
<td>76.00</td>
</tr>
<tr>
<td>1.0 g</td>
<td>88.25</td>
<td>81.75</td>
<td>80.25</td>
<td>80.00</td>
</tr>
</tbody>
</table>

### Appendix 9: Effect of temperature on mean percentage of fluoride adsorbed using SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>% fluoride ions adsorbed for SNA</th>
<th>% fluoride ions adsorbed for SNB</th>
<th>% fluoride ions adsorbed for SNC</th>
<th>% fluoride ions adsorbed for SND</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>79.00</td>
<td>81.25</td>
<td>80.75</td>
<td>62.00</td>
</tr>
<tr>
<td>40°C</td>
<td>78.75</td>
<td>81.00</td>
<td>80.25</td>
<td>61.00</td>
</tr>
<tr>
<td>50°C</td>
<td>77.00</td>
<td>80.50</td>
<td>79.50</td>
<td>59.00</td>
</tr>
<tr>
<td>60°C</td>
<td>75.25</td>
<td>77.75</td>
<td>77.50</td>
<td>58.00</td>
</tr>
<tr>
<td>80°C</td>
<td>66.50</td>
<td>76.75</td>
<td>61.00</td>
<td>54.00</td>
</tr>
</tbody>
</table>
Appendix 10: Effect of contact time on mean percentage of fluoride adsorbed using SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>Contact time (min)</th>
<th>% fluoride ions adsorbed for SNA</th>
<th>% fluoride ions adsorbed for SNB</th>
<th>% fluoride ions adsorbed for SNC</th>
<th>% fluoride ions adsorbed for SND</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min</td>
<td>75.75</td>
<td>76.00</td>
<td>80.25</td>
<td>60.00</td>
</tr>
<tr>
<td>40 min</td>
<td>79.00</td>
<td>79.50</td>
<td>80.75</td>
<td>62.00</td>
</tr>
<tr>
<td>60 min</td>
<td>80.00</td>
<td>80.00</td>
<td>80.00</td>
<td>63.00</td>
</tr>
<tr>
<td>80 min</td>
<td>80.75</td>
<td>80.50</td>
<td>81.50</td>
<td>65.00</td>
</tr>
<tr>
<td>100 min</td>
<td>82.00</td>
<td>82.00</td>
<td>82.00</td>
<td>73.00</td>
</tr>
</tbody>
</table>

Appendix 11: Effect of shaking speed on mean percentage of fluoride adsorbed using SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>Shaking speed (rpm)</th>
<th>% fluoride ions adsorbed for SNA</th>
<th>% fluoride ions adsorbed for SNB</th>
<th>% fluoride ions adsorbed for SNC</th>
<th>% fluoride ions adsorbed for SND</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 rpm</td>
<td>76.50</td>
<td>79.25</td>
<td>78.75</td>
<td>60.00</td>
</tr>
<tr>
<td>240 rpm</td>
<td>78.00</td>
<td>79.75</td>
<td>78.75</td>
<td>61.00</td>
</tr>
<tr>
<td>360 rpm</td>
<td>79.50</td>
<td>80.50</td>
<td>81.00</td>
<td>62.00</td>
</tr>
<tr>
<td>480 rpm</td>
<td>79.75</td>
<td>80.50</td>
<td>81.50</td>
<td>63.00</td>
</tr>
<tr>
<td>600 rpm</td>
<td>80.50</td>
<td>81.50</td>
<td>81.75</td>
<td>64.00</td>
</tr>
</tbody>
</table>

Appendix 12: Effect of initial concentrations on mean percentage of fluoride adsorbed using SNA, SNB, SNC and SND

<table>
<thead>
<tr>
<th>Initial ions concentrations (mg/L)</th>
<th>% fluoride ions adsorbed for SNA</th>
<th>% fluoride ions adsorbed for SNB</th>
<th>% fluoride ions adsorbed for SNC</th>
<th>% fluoride ions adsorbed for SND</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mg/L</td>
<td>75.00</td>
<td>72.00</td>
<td>66.00</td>
<td>62.50</td>
</tr>
<tr>
<td>4 mg/L</td>
<td>73.00</td>
<td>69.00</td>
<td>62.00</td>
<td>64.25</td>
</tr>
<tr>
<td>6 mg/L</td>
<td>65.00</td>
<td>65.00</td>
<td>61.00</td>
<td>65.00</td>
</tr>
<tr>
<td>8 mg/L</td>
<td>55.00</td>
<td>56.00</td>
<td>58.00</td>
<td>55.12</td>
</tr>
<tr>
<td>10 mg/L</td>
<td>54.00</td>
<td>54.00</td>
<td>56.80</td>
<td>60.00</td>
</tr>
</tbody>
</table>
Appendix 13: Langmuir adsorption isotherm for fluoride ions using SNA at 25°C

\[ y = 0.2636x + 0.1273 \quad R^2 = 0.9888 \]

Appendix 14: Freundlich adsorption isotherm for fluoride ions using SNA at 25°C

\[ y = 0.5447x + 0.3886 \quad R^2 = 0.9531 \]
Appendix 15: Langmuir adsorption isotherm for fluoride ions using SNB at 25°C

\[ y = 0.324x + 0.1118 \quad R^2 = 0.9975 \]

Appendix 16: Freundlich adsorption isotherm for fluoride ions using SNB at 25°C

\[ y = 0.6189x + 0.3483 \quad R^2 = 0.9737 \]
Appendix 17: Langmuir adsorption isotherm for fluoride ions using SNC at 25°C

\[ y = 0.4687x + 0.0719 \]
\[ R^2 = 0.9992 \]

Appendix 18: Freundlich adsorption isotherm for fluoride ions using SNC at 25°C

\[ y = 0.7943x + 0.2604 \]
\[ R^2 = 0.9981 \]
Appendix 19: Langmuir adsorption isotherm for fluoride ions using SND at 25°C

\[ y = 0.5697x + 0.0201 \]
\[ R^2 = 0.9792 \]

Appendix 20: Freundlich adsorption isotherm for fluoride ions using SND at 25°C

\[ y = 0.8561x + 0.2479 \]
\[ R^2 = 0.9445 \]
Appendix 21: Process of analysing of fluoride ions

Appendix 22: In the laboratory during the analysis of fluoride ions