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OPTIMIZATION AND CHARACTERIZATION OF SYNTHESIS CONDITIONS OF ADSORBENT FROM BONE FOR REMOVAL OF FLUORIDE

A thesis submitted to the school of Graduate Studies of Addis Ababa University presented in partial fulfillment of the requirements of the Degree of Masters of Science in Chemical Engineering

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By

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Abstract

This work aims to prepare adsorbents based on low cost cattle bones. The bones have sustained pyrolyzation in inert atmosphere at three different temperatures (400°C, 500^oC and 600°C), time (60, 90 and 120 minutes) and inlet N_2 pressure (1.5, 2 and 2.5bar) in an electric furnace. The charcoals obtained were characterized by its percentage removal of fluoride ion from synthetic fluoride water and naturally fluoridated water. The effect of contact time, adsorbent dosage, pH, temperature in shaker and initial concentration of fluoride was investigated. The adsorption was rapid during the initial one hour. The adsorption efficiency of bone char for fluoride removal was increased with adsorbent dosage. The defluoridation capacity was appreciable at neutral pH. Bone char adsorbents pyrolyzed in the range between 400 to 500^oC gave better fluoride removal. The fluoride adsorption efficiency depends directly on initial fluoride concentration. The adsorption data were well fitted to the Freundlich isotherm model. The adsorption capacity and adsorption intensity at equilibrium(q_e) are 12.075mg/g and 1.548 respectively.

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1. INTRODUCTION

1.1 Background

Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent solid. Adsorption occurs when the attractive forces at the adsorbent surface overcome the attractive forces of the liquid [1]. Adsorbent is a material used to filter harmful chemicals from contaminated water and air. As contaminated water or air flows through adsorbent, the contaminants sorb (stick) to the surface of the granules and are removed from the water or air [2].

Carbon has been used as an adsorbent for centuries. Recent changes in water discharge standards regarding toxic pollutants have placed additional emphasis on this technology [1]. Although the use of carbon-based materials dates back to ancient times, the use of activated carbon in its current form began in the second half of the twentieth century as a consequence of the rising awareness of environmental pollution. Today, activated carbon is very often utilized in the removal of various organic and inorganic species from surface water, groundwater, and waste water [3]. The primary adsorbent materials used in the adsorption process for drinking water treatment are powdered activated carbon and granulated activated carbon [4].

Bone charcoal, a mixed adsorbent containing around 10% carbon and 90% calcium phosphate, is mainly produced by thermal treatment of bones. Structurally, calcium phosphate in bone charcoal is in the hydroxyapatite form. Bone charcoal has traditionally been used in the sugar refining industry to remove color from sugar solutions [5]. Coals prepared from bones were used for a long time by food industry, for the purification of sugars, and it has proven efficiency for de-coloration of syrups, wine, vinegar, without destroying them and de-coloration of acids. This coal was also used for the removal of mercury, copper and the fluorides which can be present in abundance in water table, and used for adsorption of contaminated air and water by microbial contaminants [6].

The animal bones are composed in 65%-70% of inorganic substances, mainly hydroxyapatite. The chemical composition of hydroxyapatite is $Ca_{10}(PO_4)_6(OH)_2$. The remaining part of bones is composed of organic matter, mainly fibrous protein collagen [7].

Fluoride is an ion of the chemical element fluorine, which belongs to the halogen group. It is the most electronegative of all the elements and it is never found in elemental gaseous form except in industrial processes. Fluoride ingestion by human beings at the optimum value of between 1.0–1.5mg/l is beneficial to health (WHO 1984). The seriousness and symptoms of fluorosis vary according to the contamination level of fluoride in the consumer. Fluoride taken at concentration levels less than 0.5mg/l may result in lack of protection against dental caries, especially for children, while ingestion of between 1.5–3.0mg/l causes dental fluorosis, which is characterized by mottling and modification of the dental enamel to produce yellow and brown stains. Some studies have also reported that long term exposure to levels of between 3–6mg/l of fluoride concentrations can result in skeletal fluorosis, which is characterized by severe pain and stiffness of the backbone as well as pain in the joints. Fluoride levels beyond 10 mg/l result in crippling fluorosis, which is characterized by bending of the bones and difficulties in walking [8].

Activated carbon removes vastly more contaminants from water than does ordinary carbon [9]. Any carbonaceous waste material can be converted into activated carbon, thus its significance is two folds. Firstly, it removes pollutant from wastewater and secondly, converts solid waste into useable activated carbon [10]. There are three interfaces involved in adsorption: adsorbate–adsorbent, adsorbate–water, and water–adsorbent. Compounds that are less water soluble (hydrophobic) are more likely to be adsorbed to a solid. The lower the solubility of an adsorbate in the solvent, the higher the adsorption strength observed [10].

1.2 Problem Statement

As a result of the long-term use of high-fluoride drinking water, both dental and skeletal fluorosis is known to occur in populations from the Rift Valley. According to British geological survey, the worst cases of skeletal fluorosis are recorded at Wonji and attempts to defluoridate the water are ongoing. Dental fluorosis is also recognized in some highland communities where the water is abstracted from volcanic rocks [11]. Around 200 million people worldwide rely on drinking water that is contaminated with excess fluoride [12]. Ethiopia is one of the 23 countries where the population suffers from the consumption of fluoride rich drinking water. People in several areas of the Ethiopian Rift Valley are consuming water with up to 33mg/l of fluoride [13]. Fluorosis is known to be endemic in the Ethiopian Rift Valley. It is estimated that about 14 million people are potentially at risk of fluorosis in Ethiopia mainly in the Rift Valley area. The scarcity of surface water in the main Ethiopian Rift Valley exacerbated the vulnerability to fluorosis as the communities become highly dependent on the fluoride rich groundwater sources for drinking water supply [14]. An extensive study was done among 1,456 individuals in 14 communities in the central Rift Valley and reported dental fluorosis prevalence rates was between 69% and 98% (mean 84%) in the groups sampled [15].

In the Ethiopian Rift Valley, as elsewhere along the East African Rift Valley system, hot springs and alkaline (and saline) lakes are noted to have particularly high fluoride concentrations. Gizaw (1996) studied waters in the Lakes District of the southern Rift valley. He reported fluoride concentrations up to 60 mg/l in hot springs and ground waters from deep geothermal wells (temperatures in excess of 40℃), and fluoride in excess of 200mg/l in some of Ethiopia’s alkaline, saline lakes (Lakes Chitu, Shalla and Abayata) [16]. The basaltic rocks in that region are the main sources of fluoride. Over 40 % of deep and shallow wells are contaminated with up to 26mg/l of fluoride, a value significantly higher than the current WHO guideline of 1.5 mg/l. Mitigation of this health problem has been hampered mainly by the lack of a suitable and inexpensive removal method. Yet, fluoride removal systems in rural communities are necessary since successful implementation of such systems is still inexistent in Ethiopia [16].

City of Addis Ababa generates a solid waste of 0.4kg/c/day out of this 2% is bone waste. This could be more than 200,000t/year and about 550t/day of wastes are collected. The municipality is increasing the collection rate from 60% to 80% [17]. Accumulation of bone wastes causes environmental pollution that can be manifested in number of ways such as deterioration of the natural beauty of an environment, blockage of sewerage systems of cities and towns in developing countries which in turn creates foul smells and favorable habitats for mosquitoes and other vectors that could spread various diseases like mosquitoes.

In general, adsorbents can be prepared from any carbonaceous material. But now the researchers are exclusively using waste material/byproducts for its preparation. The benefits of using waste materials are two folds. Firstly, the raw material is available at relatively free of cost. Secondly, the waste materials get used and do not create environmental pollution [19].

Therefore the aim of this research was conducting experiment and optimizing the production conditions of adsorbent from bone for removing fluoride from drinking and waste water in order to find low cost treatment material.

1.3 Objective of the research

General objective

The general objective of this study is to perform an experimental development and optimization of production of adsorbent from bone to remove fluoride from drinking and waste water.

Specific objective

The specific objectives of this study are:

- To produce and evaluate adsorbent using bone for removal of fluoride
- To find the optimum pyrolysis temperature, time and nitrogen flow rate
- To compare different bone char products with respect to ability to adsorb fluoride
- To investigate the effect of pH on bone char adsorption capacity
- To investigate the effects of adsorbent dose, initial concentration, contact time and temperature during adsorption

1.4 Significance of the research

The significance of this study is comprised of both economy and environment. Since the adsorbent is going to be produced from bone, this study can be considered as one way of transforming a solid waste (a waste that could have been dispersed in the environment so easily) into useful material. Beside to this the produced adsorbent when it is used in drinking and waste water treatment, will contribute in keeping the countries ecosystem safer.

2. LITERATURE REVIEW

2.1 Adsorption

2.1.1 Definition

Adsorption is a mass transfer operation in which substances present in a liquid phase are adsorbed or accumulated on a solid phase and thus removed from the liquid. Adsorption processes are used in drinking water treatment for the removal of taste- and odor-causing compounds, synthetic organic chemicals, color-forming organics, and disinfection byproduct precursors. Inorganic constituents, including some that represent a health hazard, such as perchlorate, arsenic, fluoride, and some heavy metals, are also removed by adsorption [4].

2.1.2 Surface Chemistry and Forces Involved in Adsorption

Adsorption is based on the capability of porous solids with large surfaces such as silicone gel, activated carbon, etc., to selectively retain and release compounds on the surface of the solid. Two general phenomena are recognized in adsorption. Physical adsorption is a low-temperature process similar to condensation. Chemisorption, which occurs at high temperatures, is a process in which forces are very strong in the nature of an actual chemical bond [18].

There are three interfaces involved in adsorption. These are adsorbate–adsorbent, adsorbate–water, and water–adsorbent. Compounds that are less water soluble (hydrophobic) are more likely to be adsorbed to a solid. The lower the solubility of an adsorbate in the solvent, the higher the adsorption strength observed [10]. If several compounds are present in the water, strong adsorbents will attach to the carbon in greater quantity than those with weak adsorbing ability [19].

2.1.3 Nature of Adsorbents

All solids possess an adsorptive ability. However, only certain solids exhibit sufficient specificity and capacity to make an industrially useful material. Furthermore, unlike solvents for absorption, the adsorptive characteristics of solids of similar chemical composition depend mostly on their method of manufacture. All carbon is adsorptive, but only “activated” carbon is useful in industrial processes. Carbon can be activated in two ways: one is by use of a gas to create a pore structure by burning of the carbon at 700 to 1000℃ followed by treatment with steam at 700 to 900℃; the other is by removing water from the pores of uncarbonized raw materials [18].

The adsorbent must possess appropriate engineering properties, dependent on applications. If used in a fixed bed, it must not offer too great a pressure drop, nor must it be easily carried away in the flowing stream. It must have adequate strength so as not to be crushed in beds nor by being moved about in moving bed adsorbents [18].

2.2 Water and Fluoride

Water is one of the major elements essential for sustenance of all forms of life and is available in abundance in nature covering approximately three fourth of the surface of the earth. The chemical nature of water is one of the most important criteria that determines its usefulness for a specific need and as such not all the waters are fit for drinking; hence the problems of scarcity of drinking water [20]. Water related problems continue to afflict the human population the world over. Most of these afflictions are associated with contaminants of water, which extends from microbial to chemical and being both natural and anthropogenic with their effects ranging from crippling to death. The chemical contaminants include but not limited to mercury, arsenic, lead, cyanide, fluoride and sulphate ions [21]. Deprived sections of the society consume contaminated water and fall ill periodically, often resulting in epidemics. The water may be contaminated by natural sources or by industrial effluents. One such contaminant is fluoride. Fluoride is a salt of the element fluorine [22].

Fluorine is the chemical element represented by the symbol F and atomic number 9. At standard pressure and temperature, fluorine is a pale yellow gas composed of diatomic molecules, F_2. The oxidation state of the fluoride ion is -1. It is the lightest element of the halogen column of the periodic table and has a single stable isotope, fluorine-19. Fluorine is rare compared to other light elements. In Earth's crust, fluorine is more common, being the 13th most abundant element. Fluorine, a fairly common element of the earth’s crust, is present in the form of fluorides in a number of minerals and in many rocks [23]. Fluorine is a common element that does not occur in the elemental state in nature because of its high reactivity. It accounts for about 0.3g/kg of the Earth’s crust [24] and it is present in the soil and rock formation in the form of fluorapatite, fluorspar, amphiboles and micas weathering rock-alkali contribute fluoride natural waters. The fluoride present in these minerals is substituted by (OH^-) ion under redox conditions resulting in the release of fluoride ions to the circulating water [25]. Fluorine is found in the soil and the content of Fluorine in the lithosphere varies between 100 and 1500 g/ton [26].

Fluoride is highly toxic and is considered as an accumulative toxin [27]. Fluoride is present universally in almost every water body (higher concentrations are found in ground water). It is also present in most of every day needs, viz. toothpastes, drugs, cosmetics, chewing gums, mouthwashes, and so on [28]. Geological formation is the main source of fluoride in the groundwater. The other sources of fluoride occurrence in water are industrial discharge from aluminum industries, phosphate industries, coal plants as well as due to water, food, air, medicament and cosmetics [23]. Fluoride bearing rocks are fluorspar, cryolite, fluorapatite and hydroxylapatite. The fluoride content in the ground water is a function of many factors such as availability and solubility of fluoride minerals, velocity of flowing water, pH, temperature, and concentration of calcium and bicarbonate ions in water [29].

2.3 Fluoride and Human Health

2.3.1 Beneficial and harmful effects of Fluoride

Fluoride has both beneficial and harmful effects on the human health depending upon its level. Among the beneficial effects of fluoride in human body, strengthening of bones and prevention from tooth decay are significant [27]. Excessive fluoride exposure may cause irreversible demineralization of bone and tooth tissues, a condition known as fluorosis, and long-term damage to the brain, liver, thyroid and kidney [30]. Fluoride ion is attracted by positively charged calcium ion in teeth and bones due to its strong electronegativity [29].

Proxy indicators of high fluoride levels in ground water are high pH, pH beyond 7, and high sodium and bicarbonate concentrations in the water. High fluoride waters often have low calcium and magnesium concentrations as such are fairly soft [31]. About 95% of fluoride in the body is deposited in hard tissues and it continues to be deposited in calcified structure even after other bone constituents (Ca, P, Mg, carbonates and citrate) have reached the steady state. Due to such deposition, bones deformation causes irreversible damages [32].

The other problems associated with health impact of fluoride are generally overlooked because of the notion prevailing that fluoride only affects bones and teeth. Other problems arise due to the excessive intake of fluoride are fiber degeneration, low hemoglobin levels, deformities in red blood cells(RBCS), excessive thirst, headache, skin rashes, nervousness, neurological manifestation, depression, gastro intestinal problems, urinary tract malfunctioning, nausea, tingling sensation in fingers and toes, repeated abortions, male sterility etc. It is also responsible for destruction of about 60 enzymes [32]. The structural inorganic part of bones and teeth consist mainly of apatite, a mixture of more hydroxyapatite (HAP), ($Ca_{10}(PO_4)_6(OH)_2$) and less fluorapatite (FAP), ($Ca_{10}(PO_4)_6F_2$). In this structure F_2 and $(OH)_2$ are interchangeable. The parts of the apatite molecules which are FAP determine the properties of this hard tissue. At very low FAP ratios, teeth are easily soluble under acidic conditions, meaning a higher risk of dental carries. At higher FAP ratios, the solubility is reduced. However, too high a ratio causes dental fluorosis [8].

World Health Organization (WHO) and ISO: 10500 recommend that the fluoride content in drinking water should be in the range of 1-1.5mg/L. An intake of more than 6mg/d of fluoride results in multidimensional health manifestations, the most common being dental, skeletal fluorosis [28] and crippling [29]. Fluoride is “more toxic than lead and less toxic than arsenic” and is an accumulative toxin. Thus the requirement of fluoride content varies among countries and depends on the geography and the age of people involved [22]. Fluoride is more toxic than lead, and just like lead, even in minute doses, accumulates in and is damaging to brain/mind development of children, i.e. produces abnormal behavior in animals, reduces IQ in humans [29], damage to liver, thyroid and kidney [30]. Fluoride can also damage the fetus if the mother consumes water and food, with a high concentration of fluoride during pregnancy/breast feeding, infant mortality due to calcification of blood vessels can also occur. [20]

Dental fluorosis is caused by prolonged consumption of water with fluoride concentrations between 1.5 and 4.0mg/l. This is characterized by browning and mottling of teeth. Prolonged drinking of water with concentrations of fluoride between 4.0 and 10mg/l causes skeletal fluorosis and when water of concentrations beyond 10.0 mg/l is taken for a long time crippling fluorosis may ensue. Skeletal fluorosis is characterized by weakening of bones and malformation of the skeleton [31].

Symptoms of crippling fluorosis are the growing together of bone junctions causing immobility. The science behind the beneficial and harmful effects of fluoride on the skeletal structure is based on the possible ion exchange reactions between hydroxide and fluoride ions in the calcium hydroxy-phosphate, the main skeletal structure compositional material. The replacement of hydroxide ions with fluoride ions results in a more acid resistant structure, fluoroapatite [31].

$$Ca_5(PO_4)_3OH + F^- \longrightarrow Ca_5(PO_4)_3F + OH^-$$

Fluoroapatite being more resistant to acid attack compared to hydroxyapatite offers a protective layer to the tooth enamel against acids from foods. This prevents dental caries. Excessive fluoride intake however may enhance the reaction to go beyond replacement of hydroxide [31].

$$Ca_5(PO_4)_3F + 9F^- \longrightarrow Ca_5F_{10} + 3PO_4^{3-}$$

That means ion exchange occurs between phosphate and fluoride ions. The resultant compound, calcium decafluoride, is a very hard and brittle material not appropriately suited for the functions of the skeletal structure. Dental and skeletal fluorosis has however attracted greater attention as compared to the other effects of fluoride because of its obvious manifestations [31]. It may even interfere with carbohydrates, proteins, vitamins and mineral metabolism and to DNA creation as well if intake excessively [29]. The excessive fluoride intake leads to the loss of calcium from the tooth matrix, aggravating cavity formation throughout life [33].

There are many sources of fluoride in the diet. Dentists apply fluoride to teeth; some municipal water systems add fluoride to the water supply; and some toothpastes have fluoride as an additive; and some foods also have elevated fluoride such as fish and tea [34]. The requirement of fluoride content changes and it depends on the geographical condition and the age of human beings [27]. According to current knowledge, a fluoride concentration of about 0.5mg/l is beneficial in preventing dental caries during tooth development, while levels higher than 1.5mg/l may result in fluorosis or other health problems. A maximum fluoride concentration of about 4mg/l is considered adequate for the prevention of skeletal fluorosis [29].

A secondary maximum contaminant level of 2mg/l is recommended to minimize the “cosmetic” risk of dental fluorosis, which can occur when fluoride is incorporated into enamel. The World

Health Organization (WHO) guidelines suggest optimum levels of fluoride concentration at 1 and 1.5mg/l for warmer and cooler climates, respectively [29].

After oral uptake, water-soluble fluorides are rapidly and almost completely absorbed in the gastrointestinal tract. Absorbed fluoride is transported via the blood; with prolonged intake of fluoride from drinking-water, concentrations in the blood are the same as those in drinking-water, a relationship that remains valid up to a concentration in drinking-water of 10mg/liter. Distribution of fluoride is a rapid process. It is incorporated into teeth and bones; there is virtually no storage in soft tissues. Incorporation into teeth and skeletal tissues is reversible: after cessation of exposure, mobilization from these tissues takes place. Fluoride is excreted via urine, faeces and sweat. Fluoride in inhaled particles is also absorbed, the extent of absorption depending on the size of the particles and the solubility of fluoride compounds present [24]. For a total intake of 14mg/day, there is a clear excess risk of skeletal adverse effects; and there is suggestive evidence of an increased risk of effects on the skeleton at total fluoride intakes above about 6mg/day [24].

Nutritional status and physical strain also play vital role in deciding total effects of fluoride pollution. A diet poor in calcium, for example, increases the body’s retention capacity of fluoride. Environmental factors include annual mean temperature, humidity, rainfall, tropical climate, duration of exposure etc. Besides, other factors such as pH in terms of alkalinity, age, calcium in diet, fresh fruits and vitamin-C reduces fluoride toxicity. Whereas, trace elements like molybdenum enhances the fluoride toxicity [32].

2.3.2 Factors Affecting Fluorosis

The science behind the beneficial and harmful effects of fluoride on the skeletal structure is based on the possible ion exchange reactions between hydroxide and fluoride ions in the calcium hydroxy-phosphate, the main skeletal structure compositional material. The replacement of hydroxide ions with fluoride ions results in a more acid resistant structure, fluoroapatite.

$$Ca_5(PO_4)_3OH + F^- \longrightarrow Ca_5(PO_4)_3F + OH^-$$

Excessive fluoride intake however may enhance the reaction to go beyond replacement of hydroxide.

$$Ca_5(PO_4)_3F + 9F^- \longrightarrow Ca_5F_{10} + 3PO_4^{3-}$$

In the above reaction ion exchange occurs between phosphate and fluoride ions. The resultant compound, calcium decafluoride, is a very hard and brittle material not appropriately suited for the functions of the skeletal structure [31].

Skeletal fluorosis

- Severe pain in the backbone
- Severe pain in the joints
- Severe pain in the hip region
- Stiffness of the backbone.
- Immobile /Stiff joints
- Increased density of bones, besides calcification of ligaments
- Construction of vertebral canal and intervertebral foramen-pressure on nerves
- Paralysis

Non-Skeletal Manifestations

This aspect of fluorosis is often overlooked because of the misconception prevailing that fluoride will only affect bone and teeth. Fluoride, when consumed in excess can cause several ailments besides skeletal and dental fluorosis [20].

1. Neurological Manifestations

2. Muscular Manifestations

3. Allergic Manifestations

4. Gastro intestinal problems

5. Head-ache

6. Loss of teeth (edentate) at an early age

Ingestion of fluoride through food and air is relatively small compared to fluoride ingestion through water. Attention has thus been drawn to controlling fluoride concentrations in water supplied for drinking. The World Health Organization recommends that in mitigating for fluorosis in endemic areas the approach should be hierarchical in the following order; first to identify alternative source of potable water with low fluoride content, secondly to dilute high fluoride water with low fluoride water to attain a mass balance of within 1.5 mg/l, thirdly to use high calcium, magnesium and vitamin C diets and finally, when all these may not be feasible; to remove fluoride from water to meet the required level of 1.5 mg/l [31].

2.4 Defluoridation Methods

2.4.1 Definition

The process of removal of fluoride is generally termed as defluoridation. Numerous methods have been described employing various materials for the fluoride removal since 1930's [35]. Defluoridation of drinking water is the only pragmatic approach to solve the fluoride pollution problem as the use of alternate water sources and improvement of nutritional status of population at risk have their own limitations and are expensive affairs [32]. The traditional method of removing high fluoride contents from water is limiting followed by precipitation of fluoride [33]. The different methods so far tried for the removal of excess fluoride from water can be broadly classified into four categories: A) Adsorption methods, B) Ion exchange methods, C) Precipitation methods, and D) Miscellaneous methods [22].

There is a tremendous demand for removal of fluoride from drinking water. In recent years, various materials like coconut shell, tamarind seed, neem and kikar leaves, Barmuda grass neem charcoal, Moringa oleifera seed [36], fly ash, limestone, clay minerals, rare earth oxides, alumina, bone char [30], donnadialysis, electrodialysis, reverse osmosis, and nanofiltration, [37] have also been used for defluoridation. In the already established techniques for defluoridation, some technological as well as economic constraints are present. Since, calcium ions have a good affinity towards fluoride ions calcium based adsorbent such as calcite is a good alternative for defluoridation studies [38].

In recent years, nanomaterials have attracted much interest and been widely used as sorbents due to properties such as high surface-to-volume ratio and short diffusion route. Because of comparatively large surface areas, it is likely that nanosized adsorbents with strong affinity towards fluoride can be a useful tool in enhancing the adsorption capacity in drinking water treatment. However, due to their small particle size, isolation of nanosized adsorbents from matrices is difficult for practical application. Magnetic nanosized adsorbents overcome the shortcoming of nonmagnetic nanomaterials and are very promising for application in the field of preconcentration and removal pollutants from environmental samples [39].

2.4.2 Conventional methods for fluoride removal

Membrane filtration, precipitation, nanofiltration, ion-exchange, electro coagulation, flotation, reverse osmosis and adsorption have been used for fluoride removal. Most of these methods have high operational and maintenance cost, low fluoride removal capacities, lack of selectivity for fluoride, undesirable effects on water quality, generation of large volumes of sludge and complicated procedures involved in the treatment. Among these methods, adsorption is the most effective and widely used method because it is universal, has a low maintenance cost, and is applicable for the removal of fluoride even at low concentrations [29].

The common methods used for the removal of fluoride from drinking water are divided in the following four categories:

- Precipitation
- Adsorption/ion exchange methods
- Membrane filtration processes;
- Distillation.

Precipitation

Precipitation methods based on the addition of chemicals to the water is simple and economical, and is used principally for the treatment of high-fluoride containing wastewater (typically greater than 10mg/l). But, the final concentration of fluoride is generally still above level prescribed by World Health Organization (WHO) and excess chemicals in treated water are difficult to eliminate [39].

Membrane filtration process

Membrane filtration processes are among advanced water treatment technologies that have been mainly employed in treatment of pure and ultra-pure water [31]. Reverse osmosis and electrodialysis are two membrane filtration processes which can be used for removal of fluoride [40]. Reverse osmosis is an excellent choice for the reduction of fluoride [29].

Distillation

Distillation units can be used for treating the drinking water. Large scale electrodialysis plants are already used for making drinking water out of brackish water with high fluoride concentrations. In many parts of North Africa, water is brackish and contains over 1.5mg/l fluoride [40].

Reverse osmosis, electro dialysis and distillation are advanced, large scale treatment technologies which are difficult to use in less advanced regions [40].

Adsorption/ ion-exchange

Adsorption processes involve the passage of water through a contact bed where fluoride is removed by ion exchange or surface chemical reaction with the solid bed matrix. After a period of operation, a saturated column must be refilled or regenerated [36].

Adsorption seems to be economical and user-friendly especially in the developing world where point of use treatment is recommended. Different adsorbents have different limitations [37]. Adsorption is considered to be a viable approach due to its simplicity and cost-effectiveness [27].

Comparatively, adsorption seems to be the most attractive method for the removal of fluoride below 1mg/l. The criteria for the selection of adsorbent mainly include its potential (adsorption capacity) for fluoride removal and the cost. Various low-cost materials such as activated alumina, clay , soil, bone char, light weight concrete, fly ash and other materials have been tested for removing fluoride from drinking water, but the fluoride adsorption capacities of those materials are not high enough for wide application [35].

2.4.3 Defluoridation Techniques

- Precipitation methods
- Activated alumina
- Bone char
- Synthetic tricalcium phosphate

- Florex
- Activated Carbon
- Lime
- Ion Exchange Resins
- Magnesia
- Serpentine
- Lime stone, special soils and clay
- Fly Ash
- Electrocoagulation/Electrochemical methods
- Rare earth based materials
- Defluoridation by plant biomass

2.4.4 New technologies

Besides the methods mentioned above several new methods have been introduced in recent years [40]. These new technologies include:

- Crystalactor®
- Memstill® technology
- The WaterPyramid® solution
- The Solar Dew Collector system
- Boiling with brushite and calcite
- Use of new absorbents

2.4.5 Selection of adsorbent

To select a suitable defluoridation method the following criteria need to be considered [29]:

- Fluoride removal capacity

- Simple design

- Easy availability of required materials and chemicals

- Acceptability of the method by users with respect to taste and cost

2.5 Defluoridation by Bone Char

Bone char is charcoal prepared by heating animal bones at controlled temperature, heating duration and amount of oxygen. Bone char has been used as the defluoridation tool for several decades since 1940s. Since bone char is old, its use in water treatment plants in developed countries is obsolete. The fluoride removal capacity of bone char is attributed to the presence of hydroxyapatite in its structure. When fluoride ion reacts with hydroxyapatite, fluorapatite and hydroxyl ions are formed [21]. Bone char contains about 10% carbon (C) by weight with the remainder comprising mainly hydroxyapatite, ($Ca_{10}(PO_4)_6(OH)_2$) but also a significant percentage of calcium carbonate [41].

The bone charcoal (BC) residue is the result of a pyrolysis process according to the following conditions [5]:

$$\text{Cow bones} \xrightarrow{\text{pyrolysis}} \text{bone chars residue + oil + steam + liquor ammonia}$$

Bones and enamel are essentially hydroxyapatite and, in the presence of fluorides, the hydroxides are replaced by fluoride, forming a more insoluble fluorapatite. Bone char is a natural adsorbent and it has good fluoride adsorptive capacity even at neutral pH, and can be easily available [41]. The structural inorganic part of bones and teeth contains F_2 and $(OH)_2$ as interchangeable unit [8].

2.5.1 Mechanism of adsorption

Bone char ability to take up fluoride involves more than one reaction and varies with fluoride concentration, pH and available surface area. Reactions involved are direct adsorption of fluoride on the empty sites on the bone char surface. Ion exchange mechanisms where fluoride ion exchange position with OH^- or it exchanges with hydrogen carbonate/carbonate ion/phosphate ion. Recrystallisation processes where the hydroxyapatite and bone minerals dissolve and precipitate with fluoride as fluorapatite [42].

The principal reaction is:

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \longrightarrow Ca_{10}(PO_4)_6F_2 + 2OH^-$$

$$(Ca_3(PO_4)_2)_nCaCO_3 + 2F^- \longrightarrow (Ca_3(PO_4)_2)_nCaF_2 + CO_3^{2-}$$

The two charring techniques are described:

1. **Calcination** is known as a process of high temperature heating in the presence of atmospheric oxygen. The end product being pure bone mineral, a compound related to hydroxyapatite. All organic carbon material is combusted to CO_2.

2. **Pyrolysis** is a charring process with no or very limited access to oxygen. In the organic phase the bone is converted into inorganic carbon and graphite, which makes this bone char black whatever charring temperature is used. However, the fluoride uptake is mostly ascribed to the bone mineral phase (apatite).

Pyrolysed bones are therefore always totally black while calcined bones are brown-grey-white, depending of the access of oxygen and thereby degree of charring. Pyrolysis is much more fuel demanding and therefore more expensive [43].

Recently, a study presented by Dahi and Bregnhøj showed that when bone has free access to oxygen in the atmosphere (calcination), the defluoridation capacity is drastically reduced when heated at temperatures higher than 550℃. They found that pyrolysis provides the best bone char defluoridation capacity demonstrated by a linear correlation between surface area and defluoridation capacity [44].

The principal active component of bone char is $Ca_3(PO_4)_2$. Raw bone char, prepared from animal skeletons by calcination at 300-600℃ is a mixture of three macroscopically different forms i.e. black, grey, and white fragments, which exhibit considerable differences in their efficiency for defluoridation. Black bone char is best, and white bone char is ineffective for removal of fluoride [45]. Bone Char formed at lower temperatures and containing undecomposed organic matter, which may impart an unpleasant taste to the treated water. In addition, bone char is less effective when used alone in a batch method, a technique that is more appropriate where there is no reticulated (piped) water supply [45].

Investigations of bone char for fluoride adsorption has revealed that calcined bone char produced at high temperatures inhibits the adsorption process. It has though been found that bone char produced by partly calcination are suitable for adsorption provided that the charring temperatures do not exceed 500℃ and the charring time is sufficient. White types of bone char produced with a high degree of calcination are therefore regarded as unsuitable for adsorption purposes. The adsorption capacity is however unimportant in connection with contact precipitation and it has never been investigated how calcined bone char influence the processes of contact precipitation. [43].

2.5.2 Regeneration of Saturated Bone Char

The fluorapatite compound can be returned to a form suitable for repetitive fluoride adsorption with a caustic solution. These results in the formation of hydroxyapatite, with fluoride removed as sodium fluoride. Bone char reacts with fluoride by ion exchange adsorption between fluoride in the solution and carbonate of the apatite comprising bone char [8]. Studies on the use of a 1-8% solution of sodium hydroxide for the bone char regeneration have been reported [42], where the process is assumed anion exchange between the fluoride ions and the hydroxyl ions:

$$Ca_{10}(PO_4)_6F_2 + 2OH^- \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 2F^-$$

Residual caustic soda is rinsed with an acid. Behrman and Gustafson (1938) developed a carbonic acid (dissolved CO_2) method for neutralizing excess residual caustic that prolongs the active life of both tricalcium phosphate and hydroxyl apatite [42].

2.5.3 Contact Precipitation

Contact precipitation is a recently reported technique in which fluoride is removed from water through the addition of calcium and phosphate compounds. The process involves the addition of calcium and phosphate compounds to the raw water prior to its flow through the fluoride saturated bone char filter [42]. The presence of a saturated bone charcoal medium acts as a catalyst for the precipitation of fluoride either as CaF_2, and/or fluorapatite. It gives high efficiency [29]. The exact chemical process of contact precipitation are not known, but it is assumed that it is basically a combination of precipitation of fluorapatite, $Ca_{10}(P0_4)_6F_2$, and fluorite, CaF_2. Precipitation of fluorite can occur if there already are precipitated compounds to initiate the process e.g. bone char. Precipitation of fluorapatite will only occur in contact with the apatite structure in the bone char and is dependent of the pore water velocity and contact time in the filter [43].

Calcium and fluoride concentrations will decrease due to precipitation of both fluorite and fluorapatite as parallel reactions. The precipitation products depend on the concentrations of phosphate and calcium. At high concentrations both fluorapatite and fluorite will precipitate while at lower concentrations the solubility constant for fluorite will be reached and further removal of fluoride must be due to precipitation of fluorapatite alone [43]. The following reactions illustrate the removal of fluoride

$$CaCl_2.2H_2O(s) \longrightarrow Ca^{2+} + Cl^{-} + 2H_2O$$

$$NaH_2PO_4.H_2O(s) \longrightarrow PO_4^{3-} + Na^{+} + 2H^{+} + H_2O$$

$$Ca^{2+} + 2F^{-} \longrightarrow CaF_2(s)$$

$$10Ca^{2+} + 6PO_4^{3-} + 2F^{-} \longrightarrow Ca_{10}(PO_4)_6F_2(s)$$

However, if some soluble parameters are changed by the treatment process such as total phosphorus levels may exceed limits as PO_4^{3-} pH increases. Water quality taste and smell have been sometimes reported to be poor [42].

It is therefore possible that the manufacture of good quality bone char for contact precipitation is less complicated and cheaper to manufacture than bone char for adsorption [43].

2.5.4 Degreased and alkali treated bones

Degreased and alkali treated bones are effective in the removal of fluoride from initial fluoride concentration ranging from 3.5mg/l to 10mg /l to less than 0.2mg/l [20].

2.6 Fluoride Occurrence

2.6.1 Fluoride Occurrence in the World

Geogenic occurrence of fluoride is often linked to volcanic activity, fumaric gases and presence of thermal waters. Proxy indicators of high fluoride levels in groundwater are; low levels of calcium and magnesium, high levels of sodium and bicarbonate ions, and high pH above 7 [31]. Areas with high fluoride in ground water include fluoride beds encompassing parts of Iraq, Iran, Syria, Turkey, Algeria and Morocco, and the East African rift system extending from Jordan valley down through Sudan, Ethiopia, Uganda, Kenya and Tanzania. There are high fluoride areas in other parts of the world [31].

Fluoride is found in a wide variety of minerals that include fluorspar (CaF_2), cryolite (Na_3AlF_6), apatite ($Ca_5(PO_4)_3F$) and hornblende [$(Ca, Na)_2(Mg, F, Al)_5(Si, Al)_8O_{22}(OH)_2$].The average crustal abundance is known to be about 300mg/kg representing between 0.06 to 0.09% by weight of the earth crust. The presence of fluoride in ground water results from dissolution of fluoride bearing minerals where the water is in contact with a fluoritic bed [31].

2.6.2 Fluoride occurrence in East and Southern Africa

High fluoride levels occur in ground waters in some parts of Kenya, Tanzania, Malawi and The Republic of South Africa; however the East African countries have higher levels compared to the Southern Countries. Some lakes in East Africa have extremely high fluoride concentrations, an occurrence not typical in surface waters. Lake Elmentaita and Lake Nakuru of Kenya have fluoride concentrations of 1,640mg/l and 2,800mg/l respectively. The Tanzanian Lake Momella is reported to have a fluoride concentration of 690 mg/l [31].

3. MATERIALS AND METHODS

3.1 Materials and Equipments

3.1.1 Equipments

The major equipments used were tubular furnace which can operate up to a temperature of 1200℃, UV-vis spectrophotometer (HACH DR3900), water bath heater, shaker, centrifuge, oven, sieve, mechanical size reduction (mill), analytical balance, beaker plastic bottles, pH meter.

3.1.2 Chemicals

The major chemicals used were potassium fluoride (KF), hydrochloric acid, sodium hydroxide, distilled water, nitrogen gas which was used to ensure an inert atmosphere in the furnace and used as factor. The raw material for adsorbent preparation was bone waste.

3.2 Methods

3.2.1 Preparation of adsorbent

Bones that were used in this research are bones of cattle, obtained from a Burau area. At first, the bones were degreased with boiling water in a heat resistant beaker for one hour, and dried in an oven at 105℃. They were then be placed in a closed tubular reactor and introduced into a pyrolyzer at temperature (400, 500 and 600℃) in absence or limited presence of oxygen. Temperatures of up to 400℃ burning of the bone char might have been incomplete, thus resulting in less fluoride uptake by the bone char material [8]. Removal capacity at temperatures beyond 500℃ (600 – 700℃) was again reduced, which is in agreement with the hypothesis that regeneration of bone char material at high temperatures damages the hydroxyapatite structures [8]. The char were recovered after 60, 90 and 120 minutes according to the condition for each run. Charcoals were kept in closed plastic bottle to prevent any interaction with air. The pyrolyzed materials were then grinded in a grinding machine, and sieved through 1mm sieve, in order to have uniform particles.

3.2.2 Adsorbent Evaluation

The adsorbent was finally characterized for its adsorption capacity using fluoride solution. Various concentrations of fluoride solution were prepared by dissolving potassium fluoride (KF) powder in distilled water.

Fluoride for batch studies on fluoride adsorption, 100mL of fluoride solutions with initial concentrations of 1000mg/L were placed in plastic bottles to which an equal mass of 1g of the adsorbent of 1mm size was added and kept in a shaker at 25℃ for 24h to reach equilibrium. All samples were filtered prior to analysis in order to minimize interference of the adsorbent particles with the analysis. The concentrations of fluoride in the supernatant solutions before and after adsorption were determined using a UV-Visible Spectrophotometer (wave length of 5800nm) at Addis Ababa City Government, Environmental protection Authority. The amount of adsorption at equilibrium, q_e(mg/g) was calculated by the formula [30]:

$$q_e = \frac{(C_o - C_e)V}{W} \quad \ldots\ldots 3.1$$

Where, C_0 and C_e (mg/l) are the liquid-phase concentrations of the fluoride ion at initial and equilibrium state respectively; v is the volume of the solution (litre) and w is the mass of dry adsorbent used (gram).

The adsorption capacities at time t (q_t) at different concentrations are determined by:

$$q_t = \frac{(C_o - C_t)}{w} * V \quad \ldots\ldots 3.2$$

The adsorption capacity of bone char for naturally fluoridated water was also investigated following the same procedure. The batch experiments were conducted by mixing 100mL of tap water with initial concentration of 4.25mg/l collected from village near Hawassa area with bone char for 24h in 250mL plastic bottles at room temperature. After 24h shaking, the mixtures were centrifuged at 3800rpm for 15 minutes and filtered before final fluoride analysis using filter paper.

3.2.3 Effect of Pyrolysis Temperature on Adsorption

It has been cited that varying the pyrolyzing temperature, inlet nitrogen pressure and time during preparation results in charcoal with different physico-chemical characteristics and hence different adsorption properties. Hence, the charcoal samples were prepared at pyrolyzing temperature of 400℃, 500℃ and 600℃, 1.5bar,2bar and 2.5bar inlet pressure of nitrogen and pyrolyzing time of 60min, 90min and 120min. In this way, twenty different charcoal samples were prepared and their performance towards fluoride removal was investigated.

3.2.4 Effect of Pyrolysis time on the adsorption of fluoride

The effect of residence (pyrolysis) time on adsorption efficiency and capacity was investigated at 60, 90 and 120 minutes.

3.2.5 Effect of inlet nitrogen pressure on the adsorption of fluoride

The first purpose of using nitrogen is to create inert atmosphere in order to hinder side combustion reaction. The second purpose is to affect the surface of bone char in order to increase adsorption. The observed adsorption increment due to nitronen was investigated by varying nitrogen from 1.5 bar to 2.5bar.

3.2.6 Effect of Contact Time

Residual F^- concentrations were measured for different contact time of adsorption, 0.5, 1, 2, 3.5, 24, 72 hours in order to investigate the effect of contact time. In this section the kinetics of the adsorption data was also analyzed based on reaction kinetics of pseudo-first-order and pseudo-second-order mechanisms.

3.2.7 Effect of pH

Experiments were conducted to study the effect of solution pH on fluoride ion adsorption by contacting constant amount of sorbent with known constant amount of fluoride ion solution. The mixture was agitated using an incubator shaker at 200rpm and 25℃ for 60min. The pH of the solution was adjusted by the addition of 0.1M NaOH or 0.1M HCl as needed, and studies were conducted at pH 3, 5, 7 and 9. Samples were allowed to stabilize and then pH measured using an electronic pH meter. The adsorbent was then removed from the solution by centrifugation. The residual fluoride ion concentration in solution was analyzed in UV Spectrophotometer.

3.2.8 Effect of Adsorbent dose on Adsorption Capacity and Efficiency

Adsorption efficiency (i.e. percentage of adsorption) and adsorption capacity (i.e. mg of fluoride removed per gram of adsorbent) were analyzed using 1, 2 and 3 gram of bone char.

3.2.9 Effect of Initial Fluoride Concentration

The effect of initial fluoride concentration on the adsorption capacity was analyzed using different initial fluoride concentration ranging from 25 to 75 mg/l (25, 50 and 75mg/l). One grams of bone char was used at the same contact time of 60minutes.

3.3 Study Design

During charcoal production three different temperatures, residence time and inlet nitrogen pressure ranges were used. Therefore, there are three factors that were investigated in order to know optimum combination of these factors to bone adsorbent production. The experimental design on product characterization was a full factorial design. This study provided the application of response surface methodology (RSM) for optimization of the synthesis of adsorbent from bone. The influence of factors namely; pyrolysis temperature, pyrolysis time and N_2 pressure, were investigated on the response of variables such as adsorption and yield. Temperatures of up to 400℃ result in the bone char with incomplete conversion of organic matter into inorganic matter, thus resulting in less fluoride uptake by the bone char material. Removal capacity at temperatures beyond 500℃ (600 – 700℃) was again reduced, which is in agreement with the hypothesis that regeneration of bone char material at high temperatures damages the hydroxyapatite structures [8]. Nitrogen gas (N_2) pressure and pyrolysis time were determined from literature.

The effects of the following experimental factors were studied:

- Carbonization temperature
- Nitrogen gas(N_2) flow rate
- Pyrolysis time

Experimental design and Analysis

The experimental design and analysis of data, as well as the regression computations to statistically fit the response and factors into a model were used the software package Design-

Expert® 7.0. Accordingly, 20 runs were sufficient to provide information about the effect of each factor on the yield of charcoal and adsorption which were the responses.

Experimental procedure

The raw material was collected from Burau which is located near to west of Addis Ababa. The raw material was crushed into smaller size using axe and flesh was removed by washing with hot water. The crushed bone was soaked in boiling water in order to degrease at 90℃. When the water became free from grease, the bone was placed in the oven at 105℃ for one hour. Mass of 125g bone was measured for each run and introduced into the furnace. After collecting the product, the charcoal was further crushed into fine particle using grinding machine. Bone char was screened using sieve of 1mm size in order to obtain particles below 1mm. Fluoridated water was prepared using KF. Adsorption test results were analyzed for different char and conditions suspected to affect adsorption. The same procedure were followed for investigation of naturally fluoridated water.

3.4 Adsorption Isotherm Models

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species between liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species [46].

The adsorption isotherm is the most extensively employed method for representing the equilibrium states of an adsorption system. The purpose of an adsorption isotherm is to relate the adsorbate concentration in the bulk solution to the amount adsorbed at the solid/solution interface. The analysis of isotherm data is important in developing an equation which accurately represents the results and which can be used for design purposes [37]. Adsorption isotherm helps in determining the feasibility of adsorbent for treating fluoride ion in water. Freundlich and Langmuir isotherms were plotted to provide deep insight to the adsorption of fluoride on adsorbent. The isotherm not only provides the general idea of the effectiveness of the adsorbent in removing fluorides, but also indicates the maximum amount of fluoride ions that will be adsorbed by the adsorbent. However, adsorption isotherms are equilibrium tests and thus do not indicate the actual performance of the adsorbent [28].

The Langmuir and Freundlich adsorption isotherm equations are in common use for describing adsorption isotherms at a constant temperature for water and wastewater treatment application [37].

3.4.1 Freundlich Isotherm

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved [46]. It generally agrees quite well with the Langmuir equation and experimental data over moderate ranges of concentration [28].

The general form of Freundlich isotherm is given in the following equation:

$$q_e = K_f\, C_e^{1/n} \qquad 3.3$$

The linearized Freundlich adsorption isotherm is given in the following equation:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad 3.4$$

Where q_e is the amount of F^- ions adsorbed per unit weight of adsorbents (mg/g) C_e is the equilibrium concentration in solution (mg/l) K_f and 1/n are the Freundlich constants. K_f and n are the indicators of the adsorption capacity and adsorption intensity, respectively. The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of log(C_e) Vs log(q_e) was employed to generate the intercept and the slope values to determine K_f and n respectively. The magnitudes of K_f and n show easy separation of adsorbate ions from the aqueous solution and indicate favorable adsorption. The intercept K_f value is an indication of the adsorption capacity of the adsorbent; the slope 1/n indicates the effect of concentration on the adsorption capacity and represents adsorption intensity.

A smaller value of 1/n, points out a better adsorption mechanism and formation of relatively stronger bond between adsorbate and absorbent [28]. If $1/n < 1$, bond energies increases with surface density, if $1/n > 1$, bond energy decreases with surface density and if $1/n = 1$ all surface sites are equivalent [22]. The ‘n’ should have values lying in the range of 1–10 for classification as favorable adsorption. A smaller value of n indicates a weaker bond between adsorbate and adsorbent.

3.4.2 Langmuir Isotherm

Langmuir isotherm is valid for single-layer adsorption. The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane[46]. It is based on the assumption that all the adsorption sites have equal affinity for molecules of the adsorbate and there is no transmigration of adsorbate in the plane of the surface [28].

Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site [22].

The Langmuir isotherm is given by:

$$q_e = \frac{qm\, Kl\, Ce}{1+Kl\, Ce} \quad \ldots\ldots 3.5$$

The constants in the Langmuir isotherm can be determined by plotting ($1/q_e$) versus ($1/ C_e$) and making use of above equation rewritten as:

$$\frac{1}{\mathrm{qe}} = \frac{1}{\mathrm{qm}} + \frac{1}{\mathrm{qmKl}}\,\frac{1}{\mathrm{Ce}} \quad \ldots\ldots 3.6$$

Where q_m and K_l are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively. The values of q_m and K_l will be determined from the plot of $1/C_e$ Vs $1/q_e$ [46].

3.5 Adsorption Kinetics Models

The kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. To further understand the adsorption kinetics, the pseudo-second order model was used to fit the adsorption kinetic data. The pseudo-first order model was widely applied to data modeling, but no adsorption mechanisms could be reasonably available. The pseudo-second order model is based on chemical adsorption and conforms to the adsorption of fluoride on the bone char adsorbent in this study [47].

For kinetic studies, a mass of 1gram bone char was contacted with 200ml of fluoride solution having fluoride concentration of 25, 50 and 75mg/l at pH of 5.59 and shaken at 200rpm and room temperature. At predetermined intervals of times sample solutions were taken and analyzed for the final concentration of fluoride.

3.5.1 Pseudo first order kinetic model

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second order equations were applied to model the kinetics of fluoride adsorption onto bone charcoal powder. This model is also known as Largergren model, proposed in 1898, which assumes a first order adsorption kinetics and can be represented by the equation 3.7 [46].

The pseudo-first-order rate equation

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad \ldots\ldots 3.7$$

Where: q_e and q_t are adsorption capacity at equilibrium and at time t, respectively (mg/g), k1 is the rate constant of pseudo first order adsorption (1/min).

After integration and applying boundary conditions t=0 to t=t and q_t=0 to q_t=q_t, the integrated form becomes

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t \quad \ldots\ldots 3.8$$

The values of $\log(q_e - q_t)$ were linearly correlated with t. The plot of $\log(q_e - q_t)$ versus t should give a linear relationship from which k_1 and q_e can be determined from the slop and intercept of the plot, respectively. The applicability of the pseudo-first order equation to experimental data generally, differs in two ways; the parameter does not represent the number of available sites and the parameter $\log(q_e)$ is an adjustable parameter and often found not equal to the intercept of the plot $\log(q_e - q_t)$ versus t, whereas in true first order, $\log(q_e)$ should be equal to the intercept (Ho, Y.S and McKay, G. (1998)).

3.5.2 Pseudo second order kinetic model

The pseudo second-order adsorption kinetic rate equation is expressed as:

$$\frac{dqt}{dt} = K_2(q_e - q_t)^2 \text{……………………………………………………………………….}3.9$$

Where k_2 is the rate constant of the pseudo second order adsorption (g/mg.min). For the boundary conditions t=0 to t=t and q_t=0 to q_t=q_t, the integrated form of the equation becomes (the integrated rate law for the pseudo second-order reaction):

$$\frac{1}{qe-qt} = \frac{1}{qe} + K_2t \text{...}3.10$$

Equation (3.10) can be rearranged to the linear form as below (Equation3.11):

$$\frac{t}{qt} = \frac{1}{K2qe^2} + \frac{1}{qe}(t) \text{ ……………………………….…………………………...……}3.11$$

If the initial adsorption rate, h (mg/g.min) is:

$$h=K_2(q_e)^2 \text{………..……………………………..……………………………………}3.12$$

Then equation (3.11) becomes:

$$\frac{t}{qt} = \frac{1}{h} + \frac{1}{qe}(t) \text{……………………………………………………………………..}3.13$$

Table 3.1: Adsorption of synthetic fluoridated water with bone char

Std	Run	Block	Factor1 Temperature(℃)	Factor2 Time (minute)	Factor3 inlet N_2 pressure (bar)
9	1	Block1	600.0	90.0	2.0
17	2	Block1	600.0	120.0	1.5
11	3	Block1	600.0	60.0	1.5
3	4	Block1	500.0	90.0	2.0
15	5	Block1	500.0	120.0	2.0
5	6	Block1	500.0	90.0	2.5
2	7	Block1	400.0	120.0	2.5
16	8	Block1	500.0	90.0	2.0
14	9	Block1	500.0	60.0	2.0
1	10	Block1	500.0	90.0	2.0
10	11	Block1	400.0	60.0	1.5
7	12	Block1	400.0	90.0	2.0
20	13	Block1	500.0	90.0	2.0
19	14	Block1	500.0	90.0	2.0
8	15	Block1	400.0	60.0	2.5
13	16	Block1	500.0	90.0	1.5
6	17	Block1	400.0	120.0	1.5
12	18	Block1	600.0	60.0	2.5
18	19	Block1	600.0	120.0	2.5
4	20	Block1	500.0	90.0	2.0

Table 3.2: Adsorption of naturally fluoridated water with bone char

Std	Run	Block	Factor1 Temperature (℃)	Factor2 Time (minute)	Factor3 inlet N_2 pressure (bar)
9	1	Block1	600.0	90.0	2.0
17	2	Block1	600.0	120.0	1.5
11	3	Block1	600.0	60.0	1.5
3	4	Block1	500.0	90.0	2.0
15	5	Block1	500.0	120.0	2.0
5	6	Block1	500.0	90.0	2.5
2	7	Block1	400.0	120.0	2.5
16	8	Block1	500.0	90.0	2.0
14	9	Block1	500.0	60.0	2.0
1	10	Block1	500.0	90.0	2.0
10	11	Block1	400.0	60.0	1.5
7	12	Block1	400.0	90.0	2.0
20	13	Block1	500.0	90.0	2.0
19	14	Block1	500.0	90.0	2.0
8	15	Block1	400.0	60.0	2.5
13	16	Block1	500.0	90.0	1.5
6	17	Block1	400.0	120.0	1.5
12	18	Block1	600.0	60.0	2.5
18	19	Block1	600.0	120.0	2.5
4	20	Block1	500.0	90.0	2.0

As shown in the figure 3.1 pyrolysis of bone was carried out in electric furnace with temperature upto 1200℃. Heating rate, temperature and time can be adjusted using control unit.

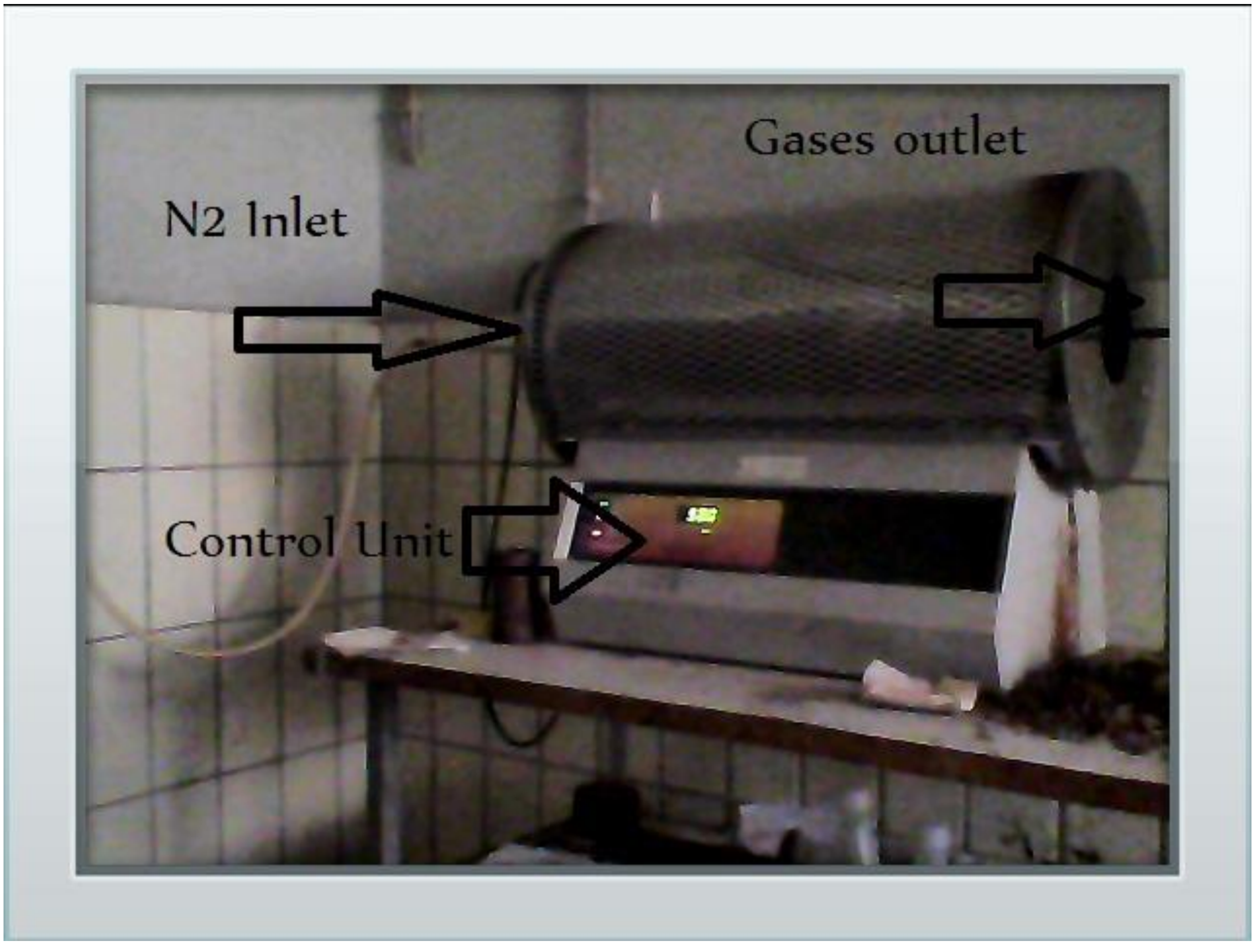

Figure 3.1 Pyrolyzer setup during bone char preparation

4. RESULT AND DISCUSSION

4.1 Effect of Parameters on Pyrolysis of Bone

Table 4.1: Adsorption and yield test result for synthetically fluoridated water

Std	Run	Block	Factor1 Temperature (℃)	Factor2 Time (min)	Factor3 inlet N_2 pressure (bar)	Response1 Yield (%)	Response2 Adsorption (%)
9	1	Block1	600.0	90.0	2.0	57.07	69.40
17	2	Block1	600.0	120.0	1.5	55.28	77.20
11	3	Block1	600.0	60.0	1.5	60.54	99.84
3	4	Block1	500.0	90.0	2.0	59.05	99.96
15	5	Block1	500.0	120.0	2.0	63.29	99.88
5	6	Block1	500.0	90.0	2.5	63.29	99.91
2	7	Block1	400.0	120.0	2.5	65.00	99.94
16	8	Block1	500.0	90.0	2.0	66.03	99.94
14	9	Block1	500.0	60.0	2.0	64.29	99.92
1	10	Block1	500.0	90.0	2.0	63.81	99.90
10	11	Block1	400.0	60.0	1.5	71.84	99.88
7	12	Block1	400.0	90.0	2.0	71.84	99.95
20	13	Block1	500.0	90.0	2.0	64.91	99.88
19	14	Block1	500.0	90.0	2.0	65.58	99.90
8	15	Block1	400.0	60.0	2.5	74.00	99.89
13	16	Block1	500.0	90.0	1.5	61.31	99.83
6	17	Block1	400.0	120.0	1.5	63.39	99.94
12	18	Block1	600.0	60.0	2.5	54.52	74.00
18	19	Block1	600.0	120.0	2.5	54.08	77.00
4	20	Block1	500.0	90.0	2.0	64.62	99.89

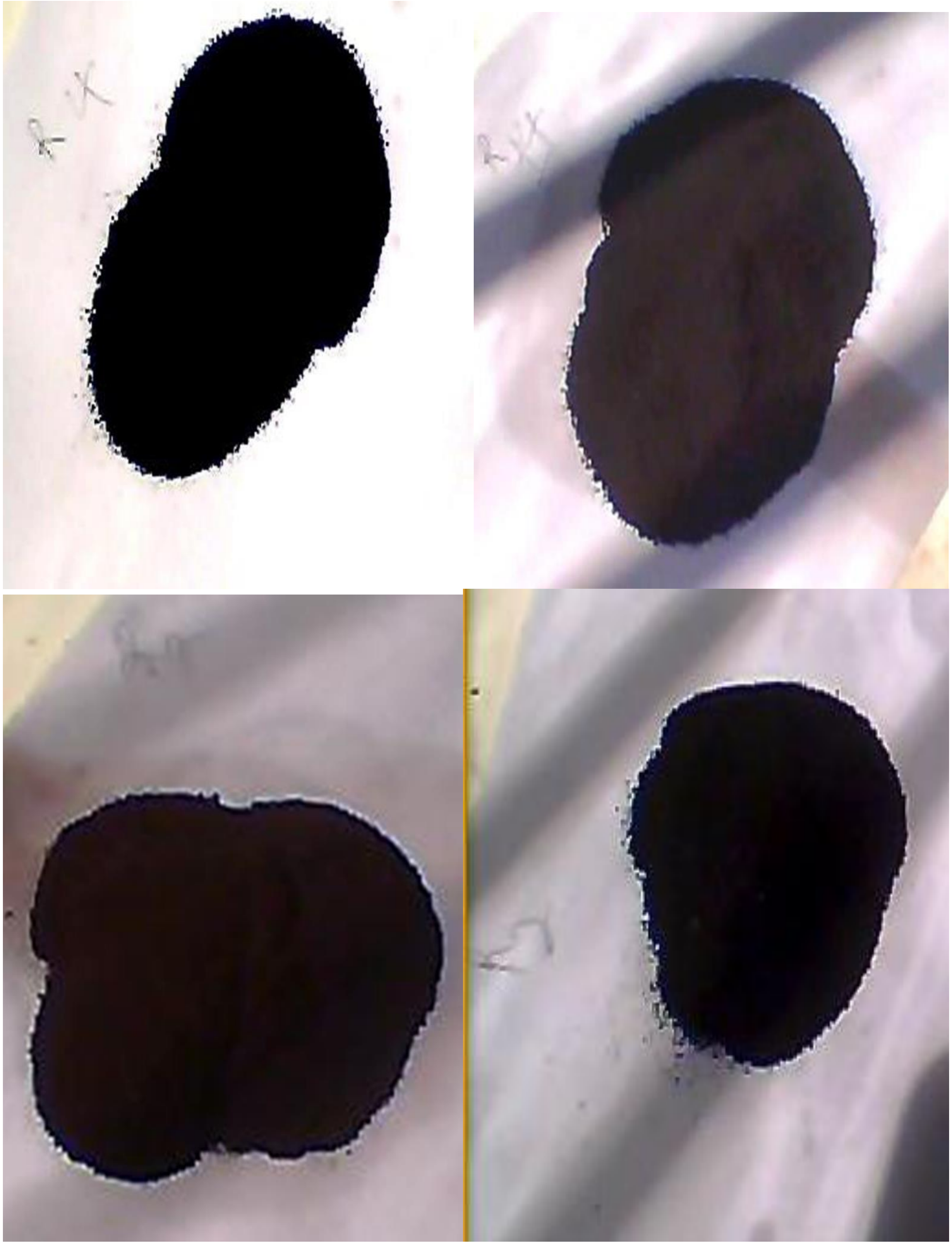

Figure 4.1 Charcoal obtained from bone at different pyrolysis conditions

4.1.1 Effect of Pyrolysis Temperature

4.1.1.1 Effect of temperature on the product yield

It has been cited that varying the pyrolyzing temperature, inlet nitrogen pressure and time during preparation resulted in charcoal with different physico-chemical characteristic and hence different adsorption properties. Hence, the charcoal samples were prepared at pyrolyzing temperature of 400℃, 500℃ and 600℃, 1.5bar, 2bar and 2.5bar inlet pressure of nitrogen and pyrolyzing time of 60min, 90min and 120min. In this way, twenty different charcoal samples were prepared and their performance towards fluoride removal was investigated.

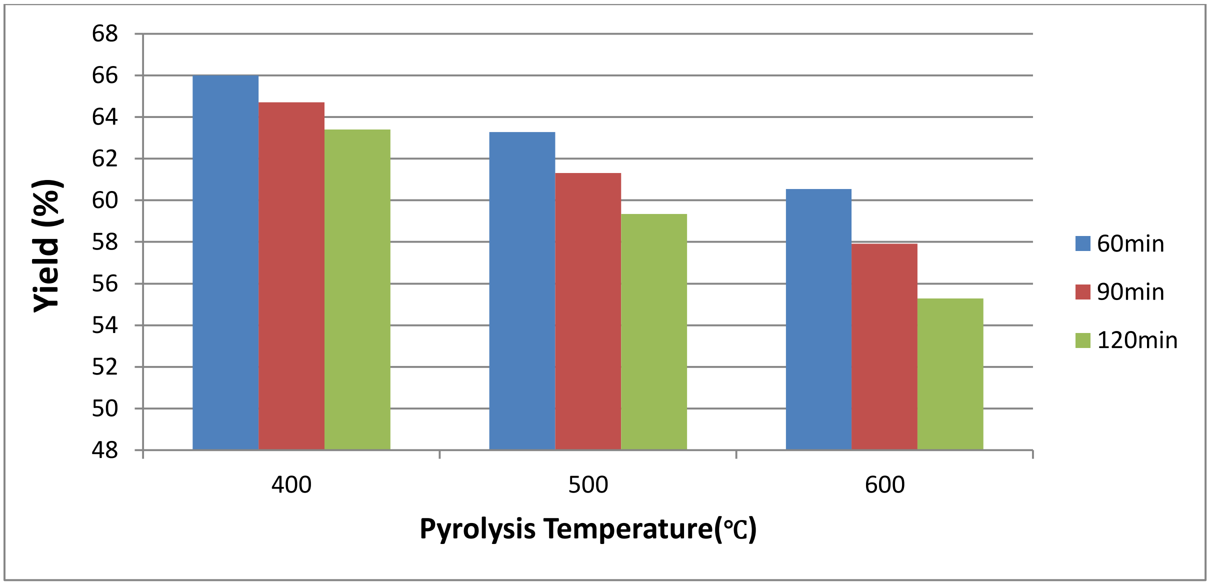

Figure 4.2 The effect of pyrolysis temperature on the yield of bone char at 1.5bar.

As shown in Figure 4.2, the final yield is strongly dependent on the operating conditions during preparation. As the temperature of pyrolysis increased, the charcoal yield decreased. The maximum charcoal yield was obtained when the bone was pyrolyzed at a temperature of 400℃. In contrast, the yield gradually decreased as the pyrolysis temperature increased. Hence, the smallest yield was obtained at an pyrolysis temperature of 600℃. This is clearly because of high temperature, releases more volatile components from the raw material.

4.1.1.2 Effect of temperature on adsorption of fluoride

The effect of pyrolysis temperature on the removal efficiency of charcoal towards fluoride is shown in Figure 4.3. The highest fluoride removal efficiency was observed for a charcoal prepared in range 400°C to 500°C and less removal efficiency was obtained for the adsorbent produced at 600°C. For temperatures up to 400°C, the bone char might be incompletely burned, thus resulting in less fluoride uptake by the bone char material. Removal capacity at temperatures beyond 500°C (600 – 700°C) was again reduced, which is in agreement with the hypothesis that regeneration of bone char material at high temperatures damages the hydroxyapatite structures [8]. The graph also shows that pyrolyzing temperature strongly affects the adsorption efficiency of bone char on flouride.

The best adsorbent was obtained at pyrolysis temperature of 500°C which resulted adsorption of 99.958%, this implies that as the temperature increased from 400°C to 500°C the volatile components were released and more vacant spaces were produced and that enhanced the adsorption capacity of the adsorbent. But, increasing the activation temperature above 500°C results in decreasing the performance of bone char, since at high temperature the hydroxyapatite structure starts to collapse and this result in losing ions that play role in ion exchange.

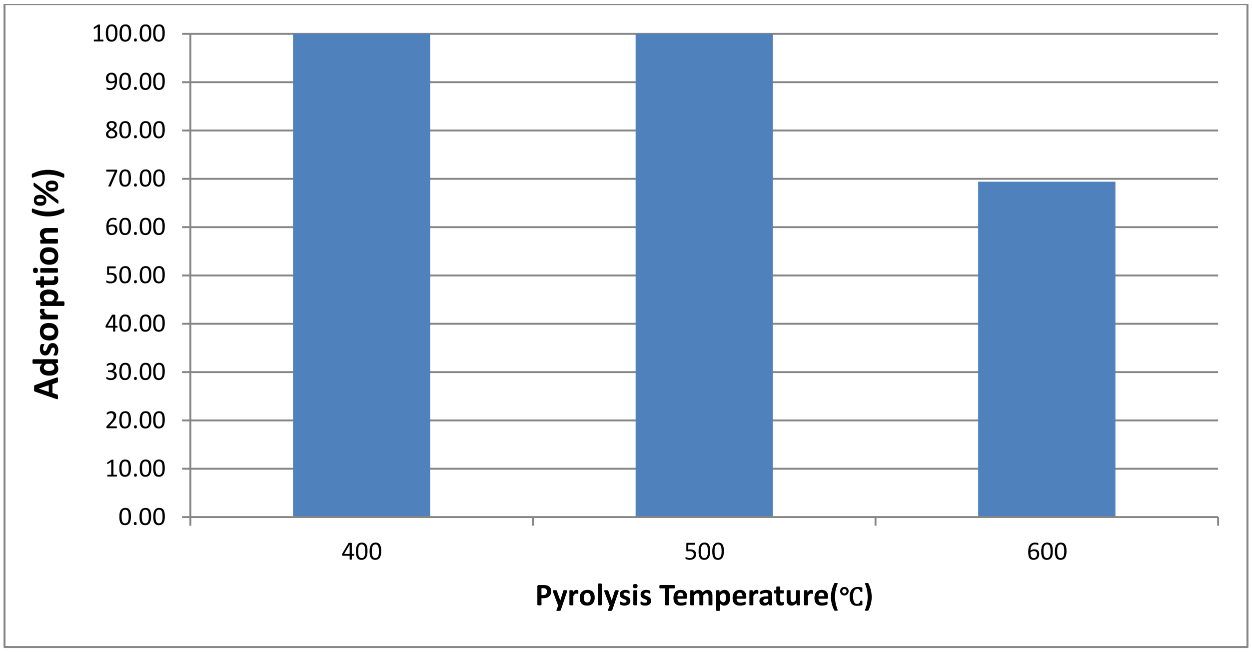

Figure 4.3 The effect of pyrolysis temperature on the adsorption capacity of bone char for fluoride ion from water at 2 bar and 90minutes.

4.1.2 Effect of Pyrolysis Time

4.1.2.1 Effect of pyrolyzing time on yield of product

Figure 4.4 shows the effect of pyrolyzing time on the yield of bone char. It is depicted that residence time has negative effect on the yield of the bone.

Comparing the yield of bone char for the different pyrolyzing times for constant pyrolyzing temperature and inlet nitrogen pressure, pyrolysis for 60 minutes resulted in high yield of bone. The less amount of bone char was collected from pyrolysis time of 120 minutes which was 54.08% of the input. The same reasons mentioned earlier for the effect of temperature on yield are considered to be the main reason here also for the decrement of yield (i.e. longer pyrolyzing time and higher pyrolyzing temperatures release more and more volatile components and this decreases the amount of bone char collected).

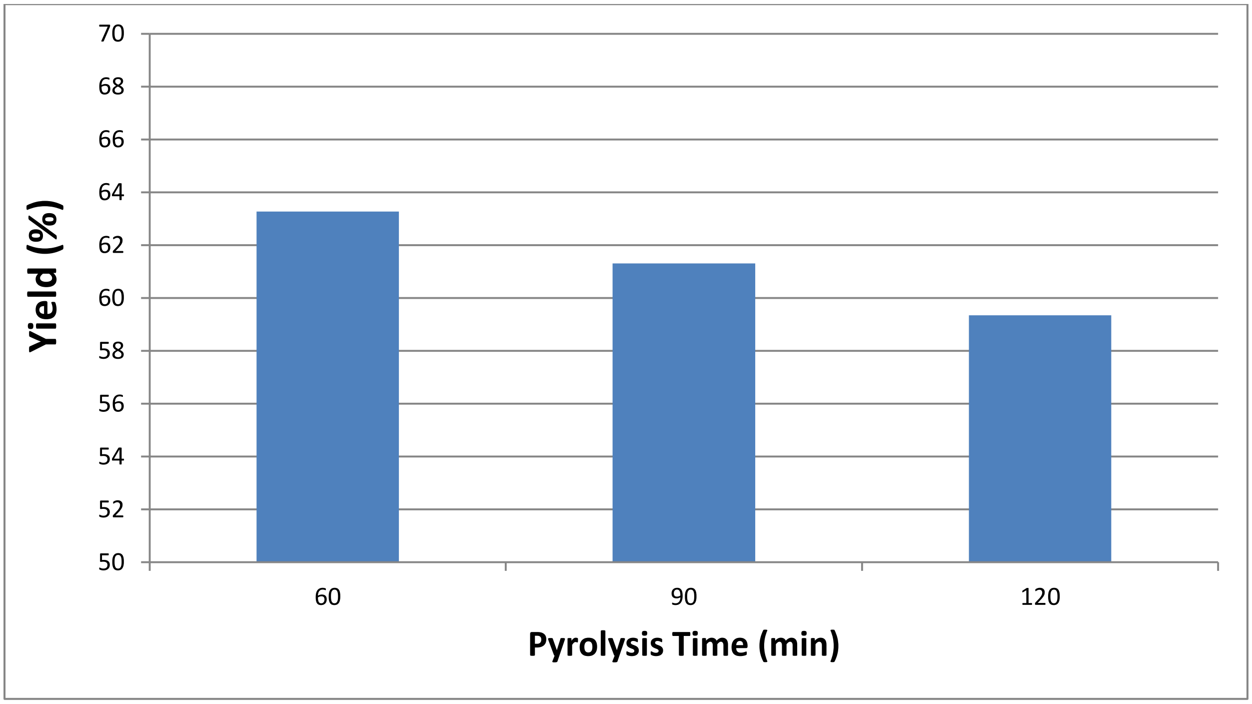

Figure 4.4 The effect of pyrolyzing time on the yield of bone char at 1.5 bar and 500℃.

4.1.2.2 Effect of Pyrolysis time on the adsorption of fluoride

Figure 4.5 shows that as the pyrolysis time increased, the percentage removal of fluoride slightly decreased at 120 minutes. Pyrolysis time of 90 minutes resulted in better adsorbent, when temperature and inlet N_2 pressure are fixed to 500℃ and 2 bar respectively. Pyrolysis times of 60 minute has shown better effects on the removal efficiency of the bone char at higher temperature. But, pyrolysis time of 120 minutes results the best adsorbent than the rest if 400℃ is chosen. The reason for this is that as bone exposure to heat increase the calcium hydroxyapatite decomposition increase, making less ion exchange possible. It is observed that the optimum pyrolysis time depends on the relative amount of temperature.

Generally, it can be seen that, the best operating condition for obtaining efficient adsorbent (charcoal) from bone is at pyrolysis time of 90 minutes.

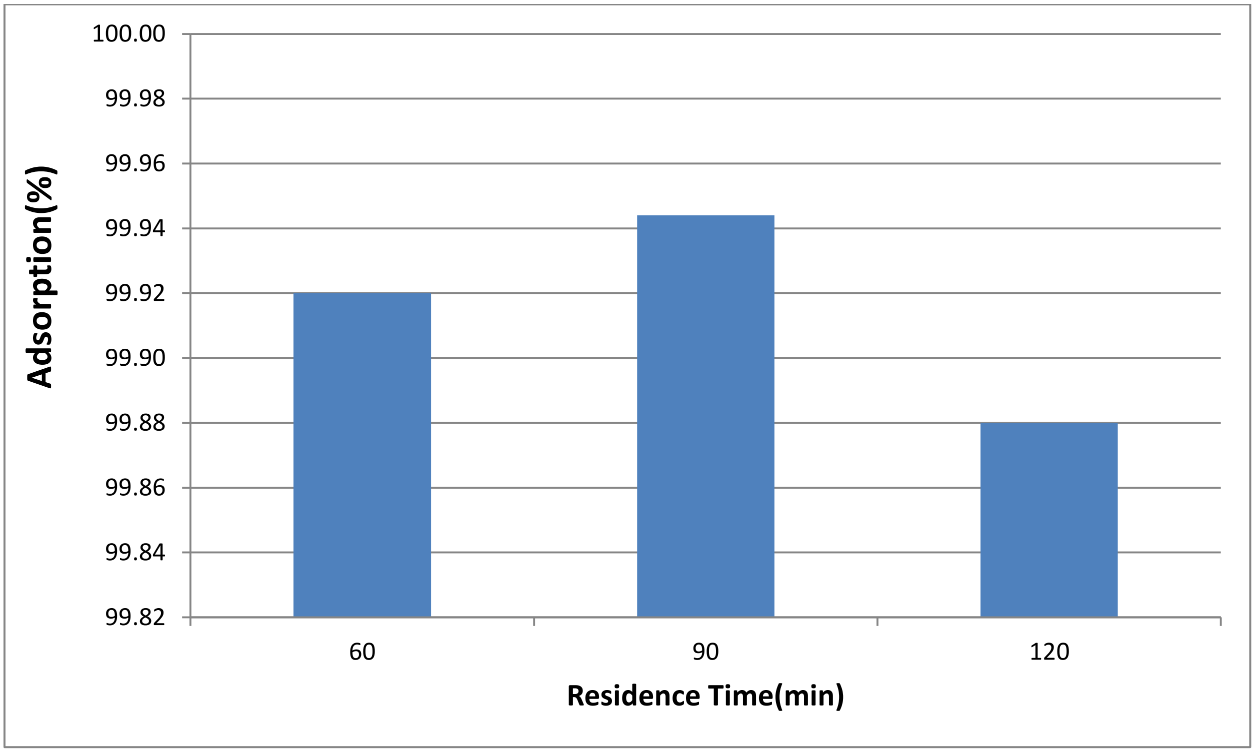

Figure 4.5 The effect of pyrolyzing time on the adsorption capacity of bone char for fluoride ion from water at 2bar and 500℃.

4.1.3 Effect of Inlet Nitrogen Pressure

4.1.3.1 Effect of inlet nitrogen pressure on product yield

The effect of inlet nitrogen pressure on the yield of bone char is shown in Figure 4.6. The effect of inlet nitrogen pressure on the yield of charcoal is observed in the figure and the yield is slightly affected by the inlet nitrogen pressure. Operating at high inlet nitrogen pressure reduce the product quantity. The maximum amount of product is obtained at the 1.5bar. The decrement on the product yield is due to the removal of more volatile components with nitrogen gas at higher pressure beyond 1.5bar.

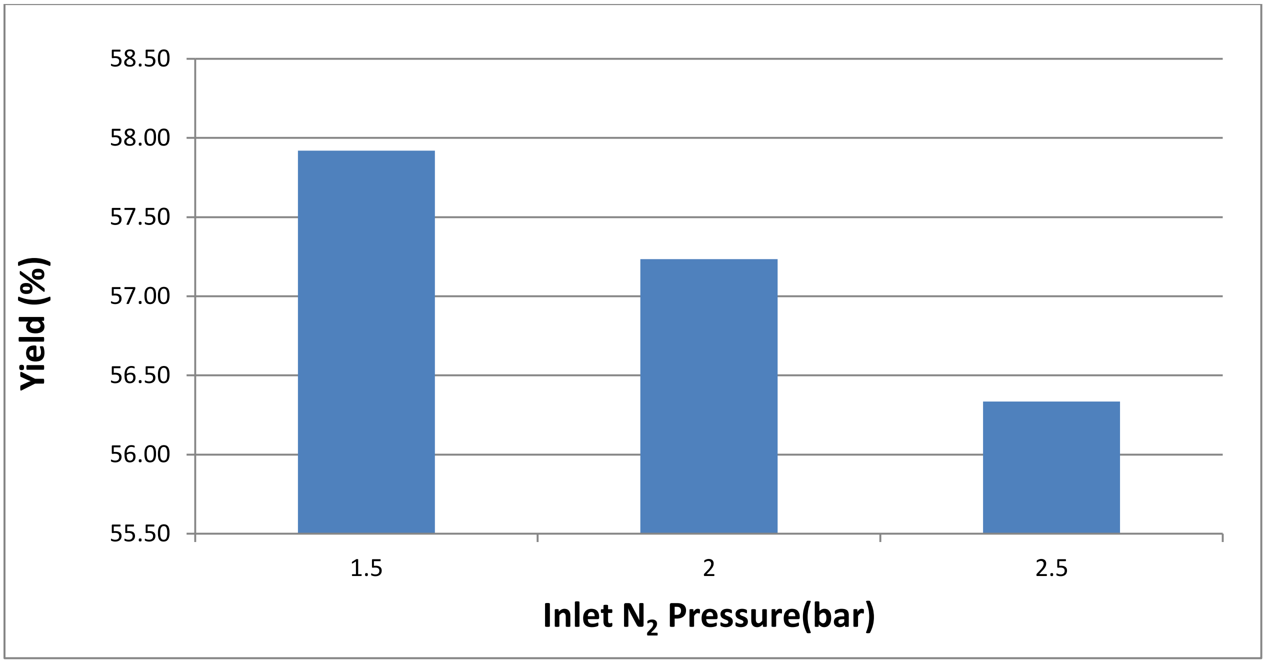

Figure 4.6 The effect of pyrolysis inlet N_2 pressure on the yield of bone char at 500℃ and 90 minutes.

4.1.3.2 Effect of inlet nitrogen pressure on the adsorption of fluoride

Figure 4.7 shows the effect of inlet nitrogen pressure on the adsorption efficiency of bone char. The figure shows that, pyrolyzing the raw material at all inlet nitrogen pressure has no significant difference for adsorption of fluoride. The first purpose of using nitrogen is to create inert atmosphere in order to hinder side combustion reaction. The second purpose is to affect the surface of bone char in order to increase adsorption. The observed adsorption increment due to nitrogen was not significant.

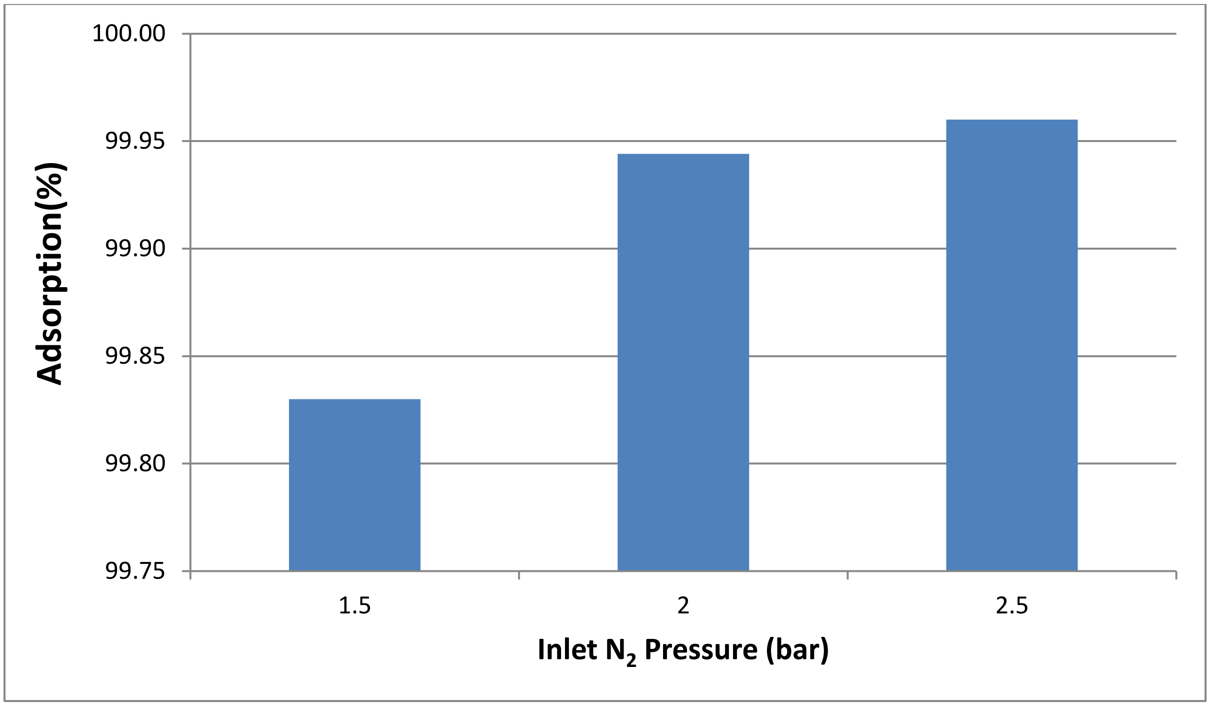

Figure 4.7 The effect of pyrolyzing inlet N_2 pressure on the adsorption capacity of bone char for fluoride ion from water at 90 minutes and 500℃.

4.2 The Effect of Contact Time

The effect of contact time on removal of fluoride using bone char is presented graphically as percentage fluoride (F^-) removal at different contact times. Contact time was found to have an effect on the amount of fluoride removed per unit weight of bone char. It may be observed from the Figure 4.8 that as contact time increases, percentage removal also increases initially and reduces gradually with time and attains almost an equilibrium condition and remains more or less constant thereafter. The fluoride concentrations in the solution continued to decrease steadily from 0 to 24 hours due to adsorption by bone char. This trend was also reported by other studies on defluoridation processes. This is due to faster saturation of the active sites with time. This implies that the bone char has specific number of active sites, which eventually are saturated after prolonged exposure to fluoride solution.

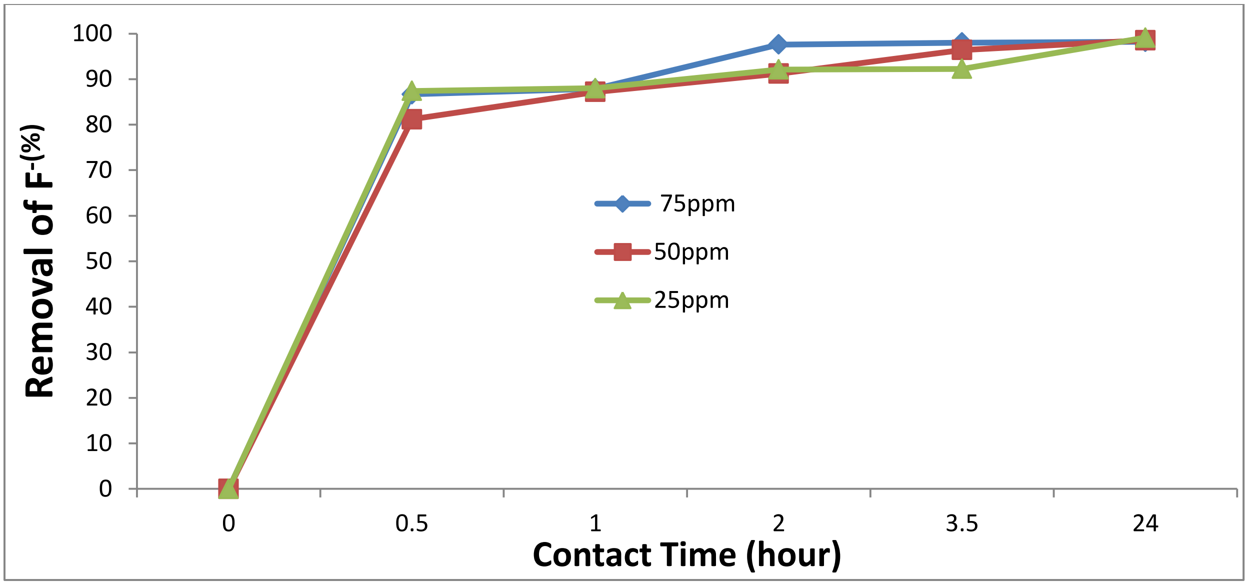

Figure 4.8 The effect of contact time on the fluoride removal efficiency.

4.3 The Effect of Bone Char Dose

Table 4.2 Dose of bone char versus fluoride removal

Dose (g per 100ml)	0	1	2	3
Remaining F^- (mg/l)	4.25	1.28	1.25	1.20
Adsorption per unit mass of char (mg/g)	-	0.297	0.15	0.102

As shown in Table 4.2 the effect of bone char dose indicated that the removal capacity of bone char for fluoride increased with increased bone char. The increase of fluoride removal with increase of bone char dose can be attributed to increasing number of active sites with increase in the bone char [41]. The lowering of the removal efficiency after 20g/l is due to possible overlapping of the active sites which masks any further increase in the dose or insufficient driving force responsible for adsorption process.

4.4 The Effect of pH

The pH at which bone char performs maximally is 7. In acidic condition, OH^- groups in the bone char can interact with H^+ in solution to form positively charged surfaces [23], thence, the ionic interaction between the bone char surface and the fluoride ion could be another way fluoride is adsorbed onto the bone char in addition to substitution of the active functional groups [41]. According to this study the pH has no significant effect on the removal capacity of bone char. Figure 4.9 shows the results obtained at pH 3, 5, 7 and 9.

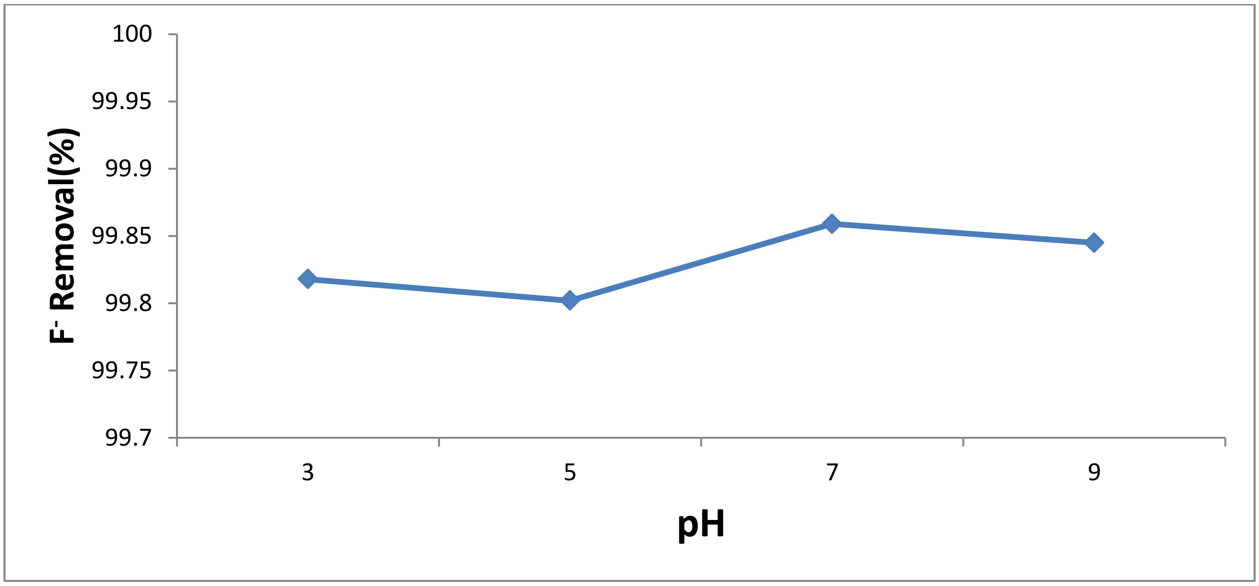

Figure 4.9 The effect of pH on fluoride removal of at 25℃, 200rpm, 1g bone char, and 60min.

4.5 The Effect of Initial Fluoride Concentration

Table 4.3: Adsorption test result for varous initial concentration and contact time

Initial concentration	Contact time (hour)				
	0.5	1	2	3.5	24
25ppm	3.15	3	1.97	1.85	0.22
50ppm	9.4	6.4	4.4	1.8	0.73
75ppm	10	9.1	1.81	1.5	1.36

The initial fluoride concentration showed influence on the removal capacity of the bone char, where the amount of fluoride adsorbed increased with increasing initial fluoride concentration from 4.4-14.728mg/g at initial concentration ranging from 25-75mg/l. This is attributable to the increased concentration gradient between the liquid and the solid phases which increasingly exceeds the mass transfer resistance between the solution and the bone char.

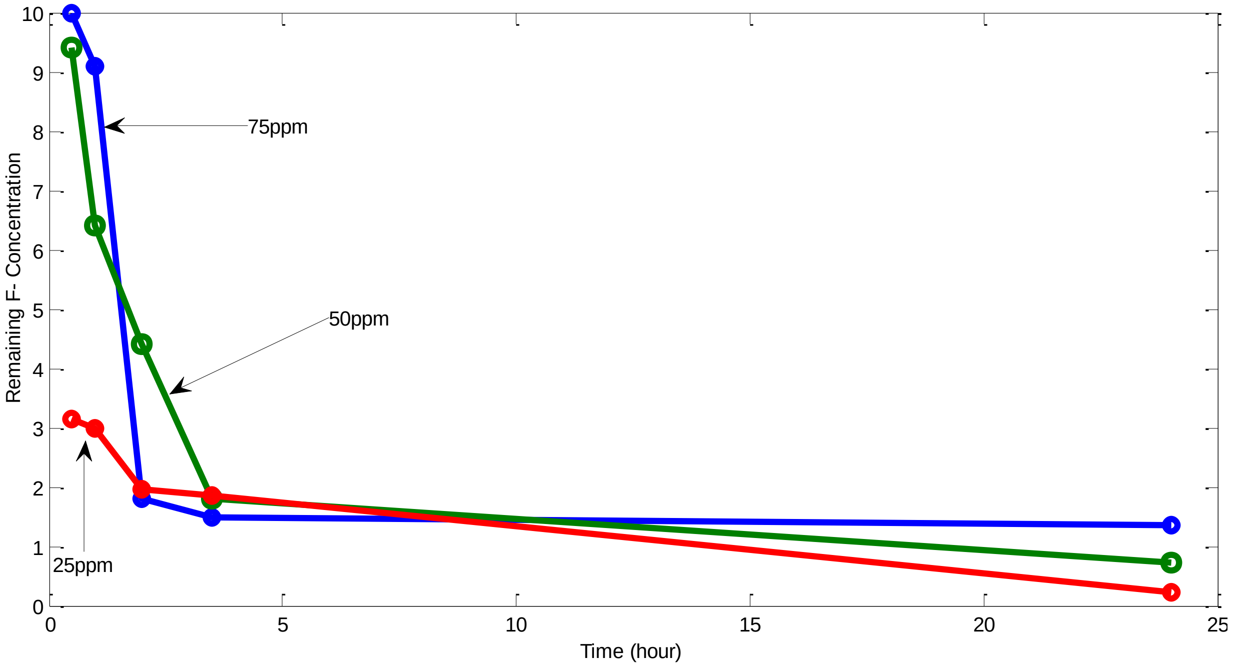

Figure 4.10 The effect of initial concentration on removal efficiency of bone char.

4.6 The Effect of Solution Temperature on Removal Efficiency

The maximum fluoride removal was seen in the range of temperature 25℃ to 30℃. The removal efficiency of bone char decreased for temperature lower than 20℃. This might be attributable to the relationship between molecular movement and temperature. As the temperature increase, the molecular movement enhanced resulting in the dissolution of the adsorbed fluoride back into the solution, in turn decreasing the amount of fluoride adsorbed. When temperature decreases the molecular movement is limited due to low kinetic energy. That decreased the chance for fluoride ion to collide with bone char so that relatively less removal was observed.

The amount of fluoride ion that was adsorbed increased at higher temperatures. This result indicated the adsorption mechanism of fluoride ion onto bone char is an endothermic reaction that means the hydroxyl and phosphate in bone char consumes heat in exchanging with a fluoride ion [48].

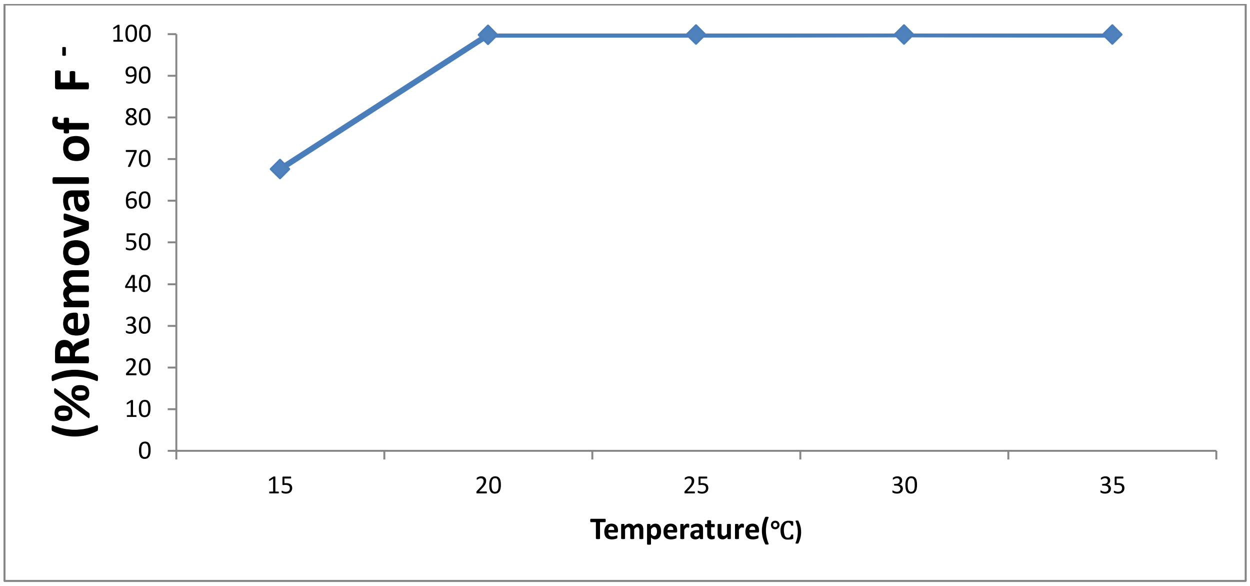

Figure 4.11 The effect of solution temperature on percentage removal of fluoride

4.7 Removal of Fluoride from Naturally Fluoridated Water by Bone Char

As an approximation of the results of the present work for application to a real problem, fluoride containing water collected from National Tobacco Enterprise S.C farm area which is located near to Hawassa, southern Ethiopia. Two different water samples were investigated to determine the amount of fluoride in the sample. The water samples were found to contain 4.25mgF$^-$/l and 4.725mgF/l. Taking the first water sample, adsorption capacity of bone char prepared under different conditions were investigated. All test results indicated in less than one mill grams of fluoride per litter (mgF$^-$/l) remaining after adsorption for contact time of 24 hours. Fluoride ions were analyzed by UV spectrometer (HACH, DR-3900). Analysis for fluoride in the final time indicated maximum 100% removal of the ions originally present in the samples. The minimum removal was 77.18% for F$^-$. These results show that bone char is a suitable material for the removal of this ion. The result of percentage removal is given below in the Table 4.4.

Table 4.4: Adsorption test result for naturally fluoridated water

Std	Run	Block	Factor1 Temperature (°C)	Factor2 Time (min)	Factor3 Inlet N_2 pressure(bar)	Response2 Adsorption (%)
9	1	Block1	600.0	90.0	2.0	100.00
17	2	Block1	600.0	120.0	1.5	86.12
11	3	Block1	600.0	60.0	1.5	100.00
3	4	Block1	500.0	90.0	2.0	83.53
15	5	Block1	500.0	120.0	2.0	77.18
5	6	Block1	500.0	90.0	2.5	100.00
2	7	Block1	400.0	120.0	2.5	100.00
16	8	Block1	500.0	90.0	2.0	100.00
14	9	Block1	500.0	60.0	2.0	96.47
1	10	Block1	500.0	90.0	2.0	80.24
10	11	Block1	400.0	60.0	1.5	89.88
7	12	Block1	400.0	90.0	2.0	100.00
20	13	Block1	500.0	90.0	2.0	91.53
19	14	Block1	500.0	90.0	2.0	93.41
8	15	Block1	400.0	60.0	2.5	100.00
13	16	Block1	500.0	90.0	1.5	80.47
6	17	Block1	400.0	120.0	1.5	90.82
12	18	Block1	600.0	60.0	2.5	100.00
18	19	Block1	600.0	120.0	2.5	86.12
4	20	Block1	500.0	90.0	2.0	95.77

The maximum fluoride required in drinking water according to World Health Organization (WHO) is 1.5mg/l. This requirement can be achieved by 70% removal capacity of bone char since 70 percent of 4.725mg/l is below 1.5mg/l. Hence bone char produced at any combination of temperature, time and nitrogen gas pressure within the boundary used in this research satisfied this requirement. The adsorption results given in Table 4.4 indicated that minimum removal obtained was 77.18% which is greater than the required 70 percent removal. It was also seen that as the amount of fluoride increase bone char can reduce the amount of fluoride into requirement.

The result obtained for naturally fluoridated water differs with that of synthetically fluoridated water for some points. The reason for this might be attributed to the presence of other ions competing with fluoride for active site. The condition resulting low fluoride removal, it may be the best condition for other ion removal in prefers to fluoride ion.

Therefore, problems like National Tobacco Enterprise S.C and other rift valley area can be solved by using bone char with appropriate equipment design for bed support.

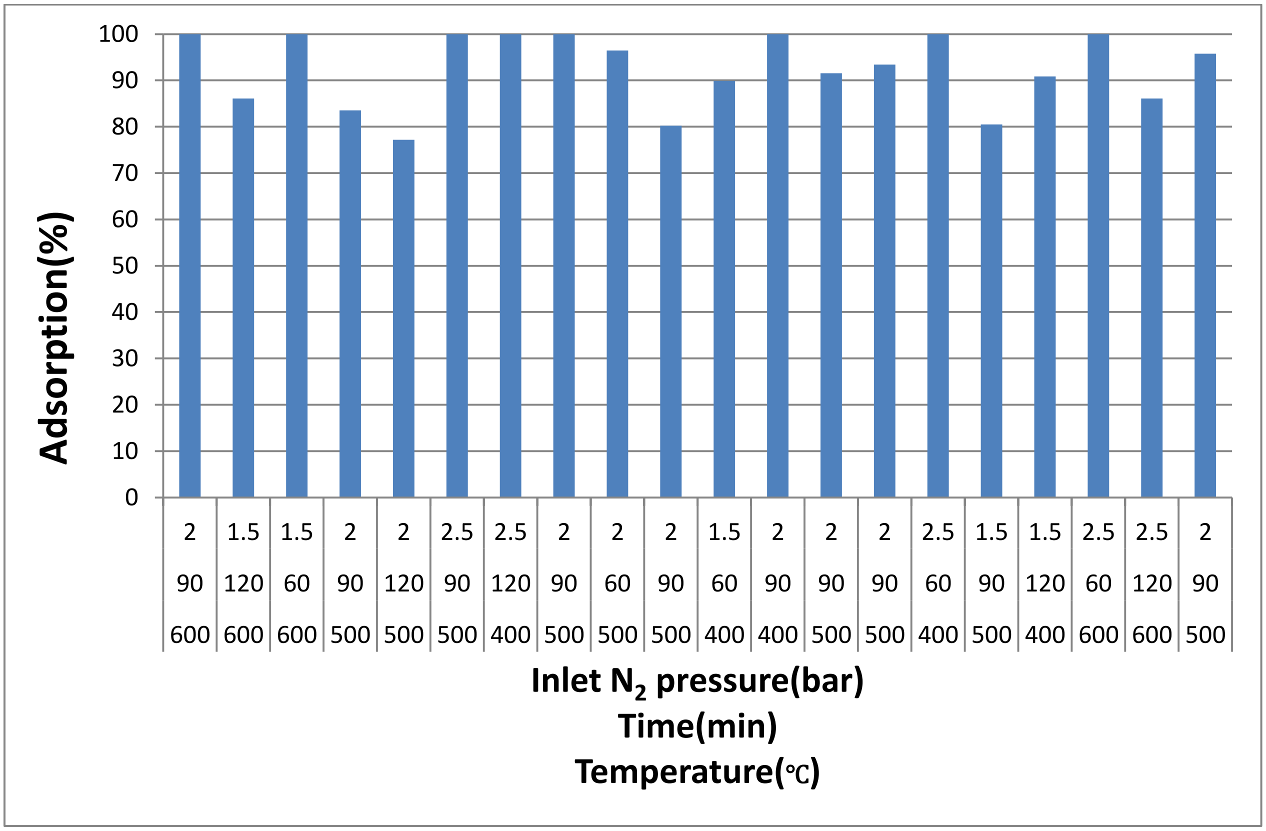

Figure 4.12 The adsorption capacity of bone char for naturally fluoridated water.

4.8 Optimum Pyrolysis Condition

The optimization of the production conditions of bone char adsorbent from bone was done by using response surface methodology (RSM). The effect of pyrolysis temperature, pyrolysis time and inlet N_2 pressure were investigated on the responses of yield and adsorption. Variance analysis (*ANOVA*) of the obtained quadratic model showed that the significant factors for adsorption and yield were temperature and time. The optimal conditions found from the RSM were temperature of 400℃ to 550℃, time of 60 to 90minutes and inlet N_2 pressure of 1.5bar, resulting in bone char with 99% fluoride removal, yield greater than 60%. Adsorption is our main response so that the optimum condition determined based on adsorption result found in the range 400 to 550℃ for temperature, 60 to 90minutes for time and 1.5bar for inlet N_2 pressure. In order to avoid the unwanted color and taste due to organic components of the bone and at the same time to obtain greater adsorption for fluoride, it is better to prepare the bone char at condition that convert all organic matter into inorganic matter.

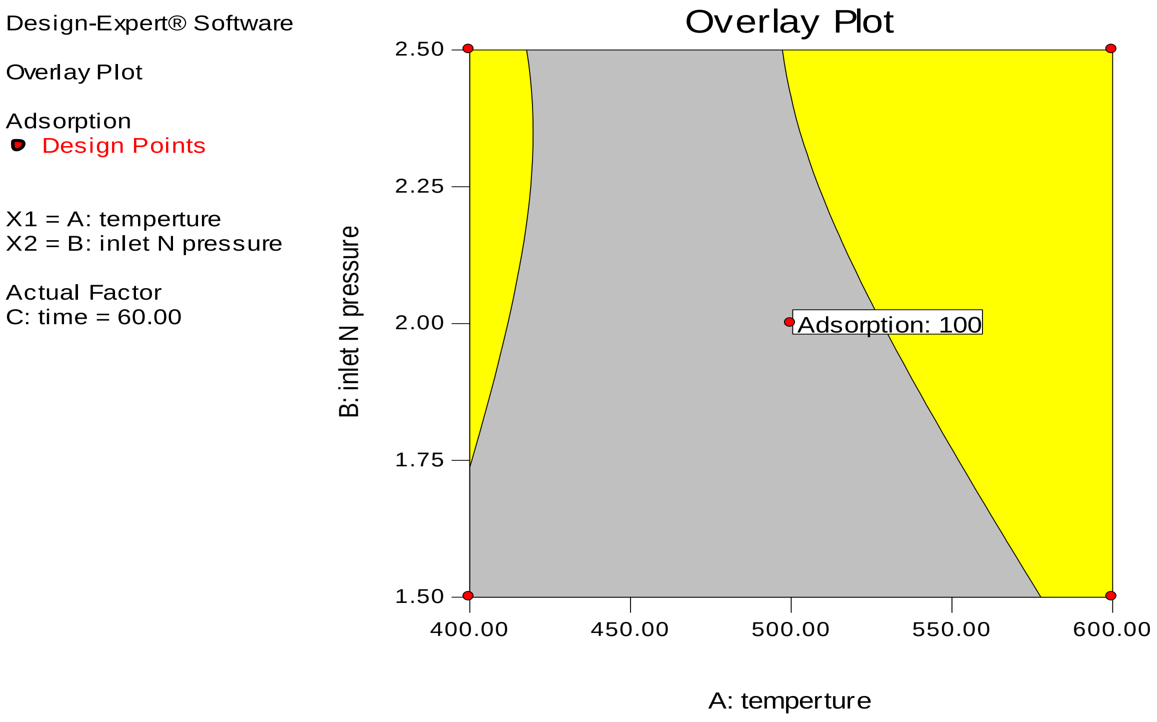

Figure 4.13 Optimum fluoride removal region

As shown in the Figure 4.13 the maximum adsorption obtained in the region shadded with grey color. Optimization by response surface methodology gave 100% adsorption in the grey region. All factors namely temperature, time and nitrogen minimized at lower left part of grey region. But in order to hinder the effect of color and taste it is better to choose optimum point at 500℃, 60 minutes and 1.5bar.

Final Equation in Terms of Actual Factors:

Yield =+80.42195-0.14948x(temperture)+62.54366x(Inlet N_2 pressure)-0.45478x(time) -0.027482x(temperture)x(Inlet N_2 pressure)+4.89875x10^{-4}x(temperture)x(time) +0.035608x(Inlet N_2 pressure)x(time)+9.57727x10^{-5}x(temperture)^2 -13.28709x(Inlet N_2 pressure)^2+3.23030x10^{-4}x(time)^2

Final Equation in Terms of Actual Factors:

Adsorption = -163.79239+1.39590x(temperture) - 28.31309x(inlet N pressure) - 0.53841x(time) -0.065103x(temperture)x(inlet N pressure) - 8.22542x10^{-4}x(temperture)x(time)

+0.21359x(inlet N pressure)x(time) - 1.29382x10^{-3}x(temperture)^2

+ 9.11527x(inlet N pressure)^2 + 2.54035x10^{-3}x(time)^2

4.9 Adsorption Isotherm Models

4.9.1 Langmuir isotherm model

The constants in the Langmuir isotherm can be determined by plotting ($1/q_e$) versus ($1/ C_e$) and making use of Langmuir equation rewritten as:

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{qmKl}(1/C_e) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4.1$$

Where q_m and K_l are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively. The values of q_m and K_l will be determined from the plot of $1/C_e$ Vs $1/q_e$.

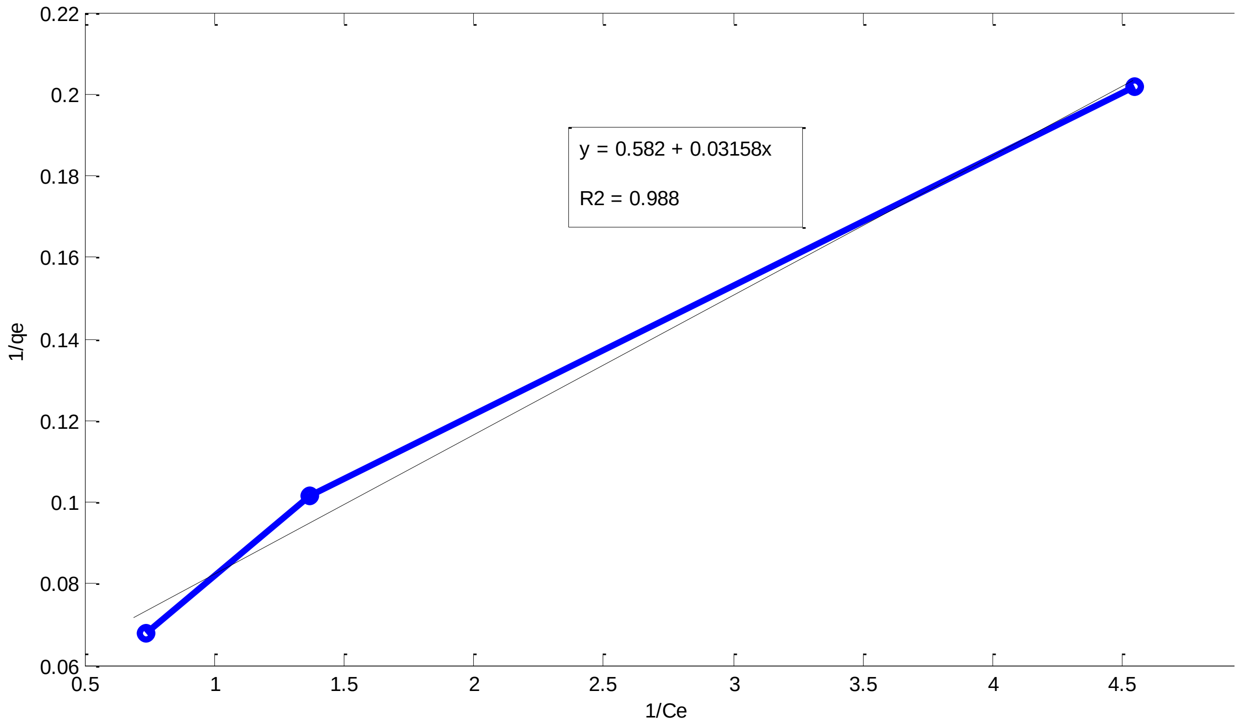

Figure 4.14 Langmuir isotherm model curve

4.9.2 Freundlich isotherm model

Freundlich adsorption isotherm is the relationship between the amounts of fluoride adsorbed per unit mass of adsorbent, q_e, and the concentration of fluoride at equilibrium, C_e is related to q_e as shown below.

$$\mathbf{q_e = K_f C_e^{1/n}} \quad \ldots\ldots 4.2$$

The logarithmic form of the equation becomes,

$$\mathbf{\log q_e = \log K_f + \frac{1}{n} \log C_e} \quad \ldots\ldots 4.3$$

The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of $\log(C_e)$ Vs $\log(q_e)$ was employed to generate the intercept value of $\log K_f$ and the slope of 1/n.

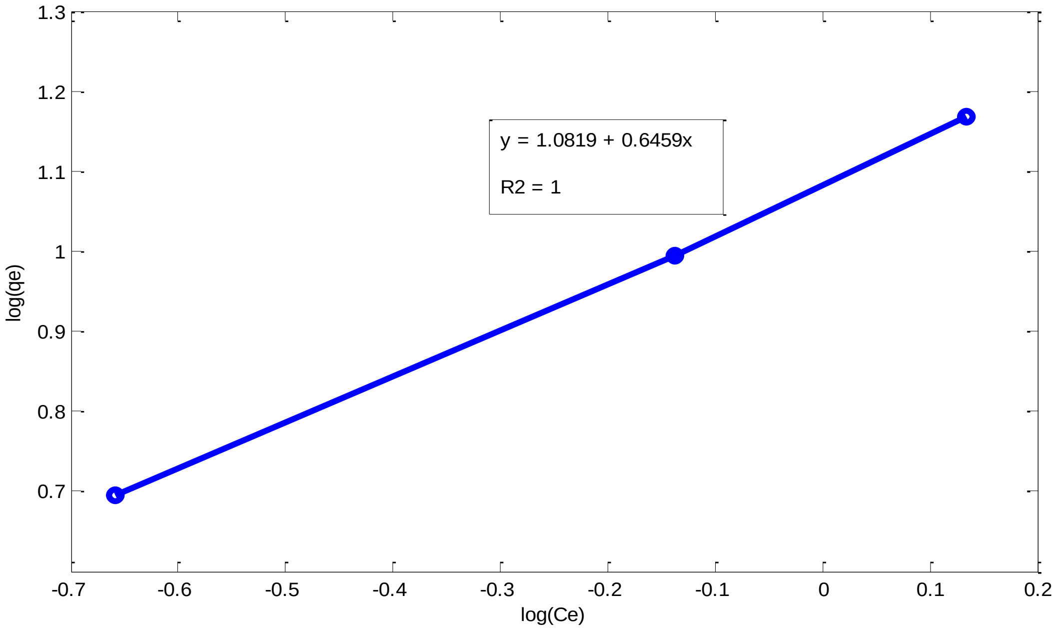

Figure 4.15 Freundlich isotherm model curve

The constant parameters for the Langmuir and Freundlich models are calculated and presented in Table 4.5. From the table it can be concluded that the Freundlich isotherm model best fits for the product. The R^2 value of the Langmuir model for the bone char is 0.988 and R^2 value of the Freundlich model for the bone char is 1. It is evident from a comparison of the values of coefficient of correlation (R^2) that the equilibrium adsorption of fluoride on to bone char follows Freundlich adsorption isotherm model which reflects adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved [46]. Based on these results, it can be inferred that fluoride is effectively adsorbed on bone char and that the Freundlich model provides a satisfactory description of the adsorption equilibrium.

Therefore, Freundlich model is selected to be the best model for describing the adsorption of fluoride by the bone char. The adsorption capacity and adsorption intensity for the Freundlich model at equilibrium (q_e) are 12.075mg/g and 1.548 respectively.

Table 4.5: Adsorption isotherm model parameters

Freundlich Model	Langmuir Model
K_f =12.0752mg/g	q_m =34.388mg/g
N =1.5483	K_l =1.8157L/mg
R^2 =1	R^2 =0.988

4.10 Adsorption Kinetics Models

The kinetics of adsorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. The pseudo-first order and pseudo-second-order kinetic models were used to investigate the adsorption kinetics of fluoride and to quantify the extent of uptake in the adsorption process. It is one of the important characteristics in defining the efficiency of sorption. In the present study, the kinetics of F^- ion removal was carried out to understand the behavior of prepared low cost bone char adsorbent and the corresponding data was given in Table 4.6 and 4.7.

4.10.1 Pseudo first order kinetics model

$$\log(q_e - q_t) = \log(q_e) - \frac{K1}{2.303}t \qquad 4.4$$

The values of log ($q_e - q_t$) were linearly correlated with t. The plot of log ($q_e - q_t$) versus t should give a linear relationship from which k_1 and qe can be determined from the slop and intercept of the plot, respectively.

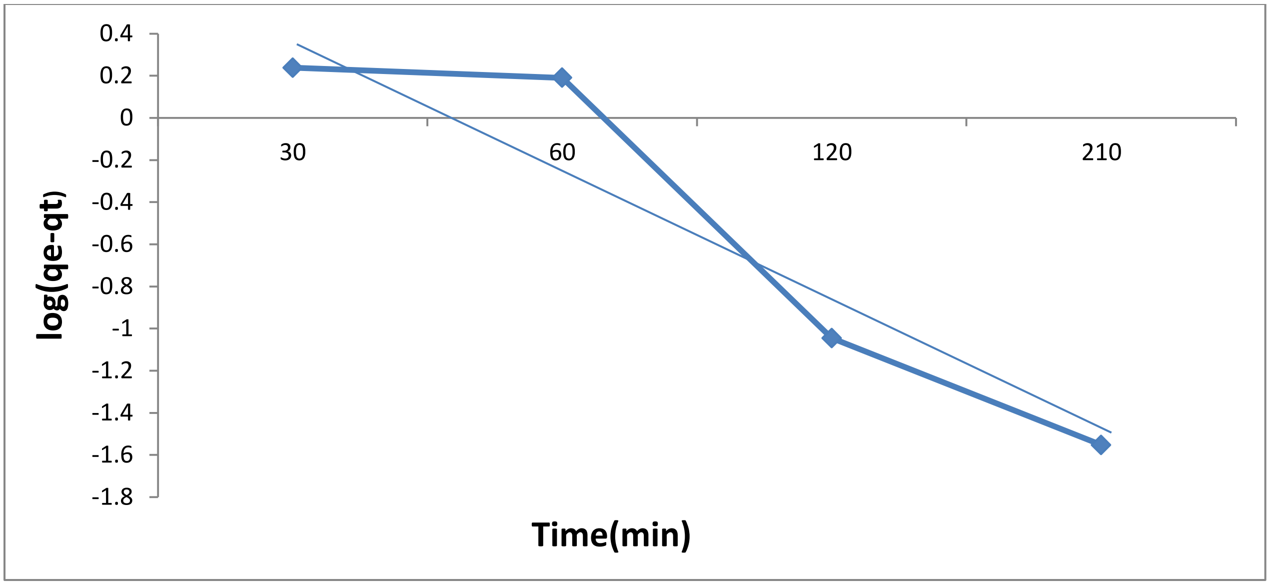

Figure 4.16 Pseudo first order kinetics curve for 75ppm

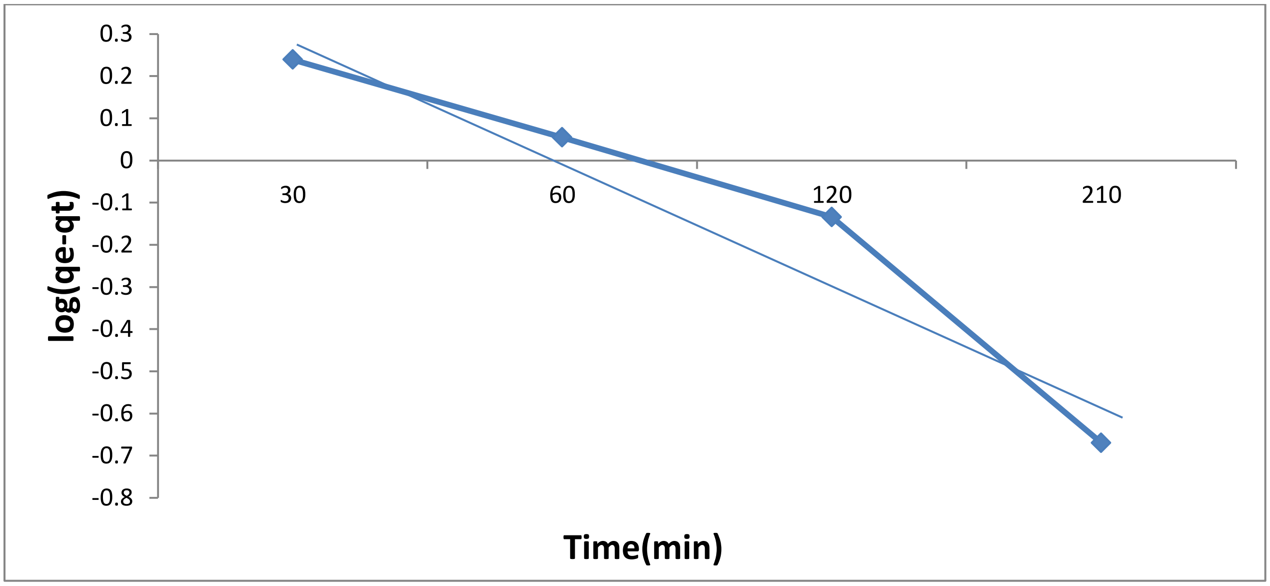

Figure 4.17 Pseudo first order kinetics curve for 50ppm

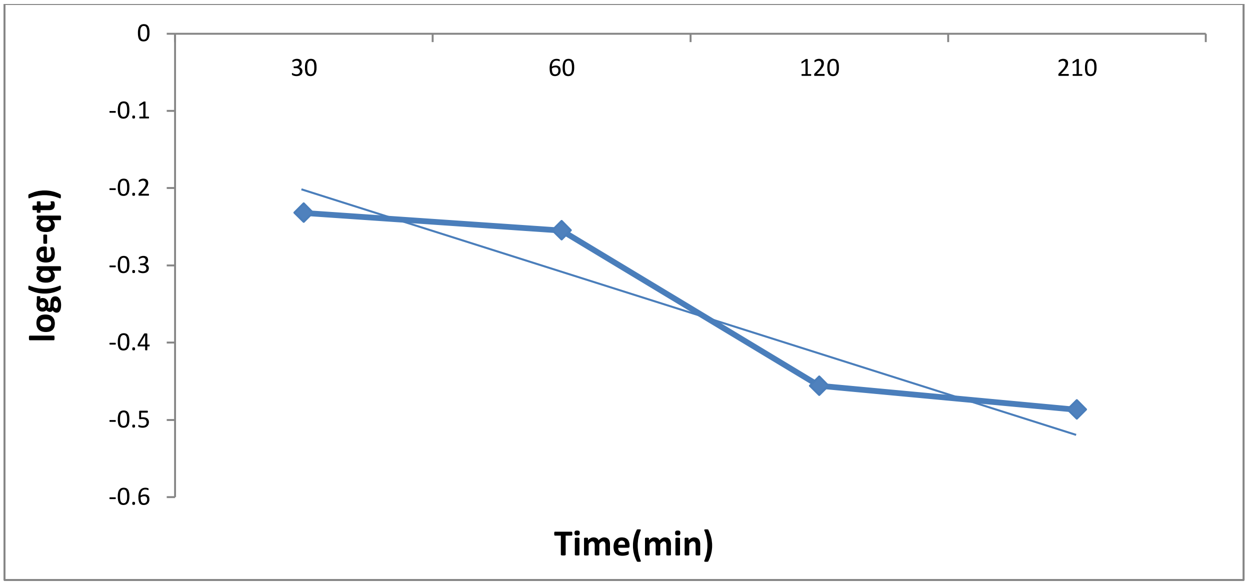

Figure 4.18 Pseudo first order kinetics curve for 25ppm

The kinetics model for pseudo first order adsorption is given for the bone char. The different parameters of pseudo first order kinetics are given in Table 4.6, from the table comparing the correlation coefficients of pseudo first and pseudo second order kinetics the best kinetics that fits the experimental data is preferably selected.

Table 4.6: Pseudo first order kinetics model data

Time (min)	Initial fluoride concentration (75ppm)		Initial fluoride concentration (50ppm)		Initial fluoride concentration (25ppm)	
	q_t(mg/g)	Log(q_e-q_t)	q_t(mg/g)	Log(q_e-q_t)	q_t(mg/g)	Log(q_e-q_t)
30	13	0.238	8.12	0.2391	4.37	-0.2321
60	13.18	0.1898	8.72	0.0546	4.4	-0.2549
120	14.638	-1.0458	9.12	-0.1343	4.606	-0.4559
210	14.7	-1.553	9.64	-0.6696	4.63	-0.4868
1440	14.728	----	9.854	-----	4.956	----
4320	14.728	----	9.854	----	4.956	-----
Pseudo First order Kinetics	75ppm	Intercept (log q_e)	1.607			
		K_a	$3.7x10^{-3}$			
		R^2	0.04			
	50ppm	Intercept (log q_e)	0.4236			
		K_a	0.0142			
		R^2	0.0012			
	25ppm	Intercept (log q_e)	-0.2093			
		K_a	$1.75x10^{-3}$			
		R^2	0.718			

4.10.2 Pseudo second order kinetics

The pseudo second-order adsorption kinetic rate equation is expressed as:

$$\frac{dqt}{dt} = K_2(q_e - q_t)^2 \text{ ……………………..…………………………………………4.5}$$

Where: k_2 is the rate constant of the pseudo second order adsorption (g/mg.min). For the boundary conditions t=0 to t=t and q_t=0 to q_t=q_t, the integrated form of the equation becomes (the integrated rate law for the pseudo second-order reaction):

$$\frac{t}{qt} = \frac{1}{h} + \frac{1}{qe}(t) \text{……………..…………………………………………………..4.6}$$

The plot of (t/q_t) and t of equation (4.6) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

Similar to the pseudo first order kinetics, here also the experimental data are plotted in a graph as shown below, then from the given curves the parameters for pseudo second order kinetic model are calculated and put in a Table 4.7.

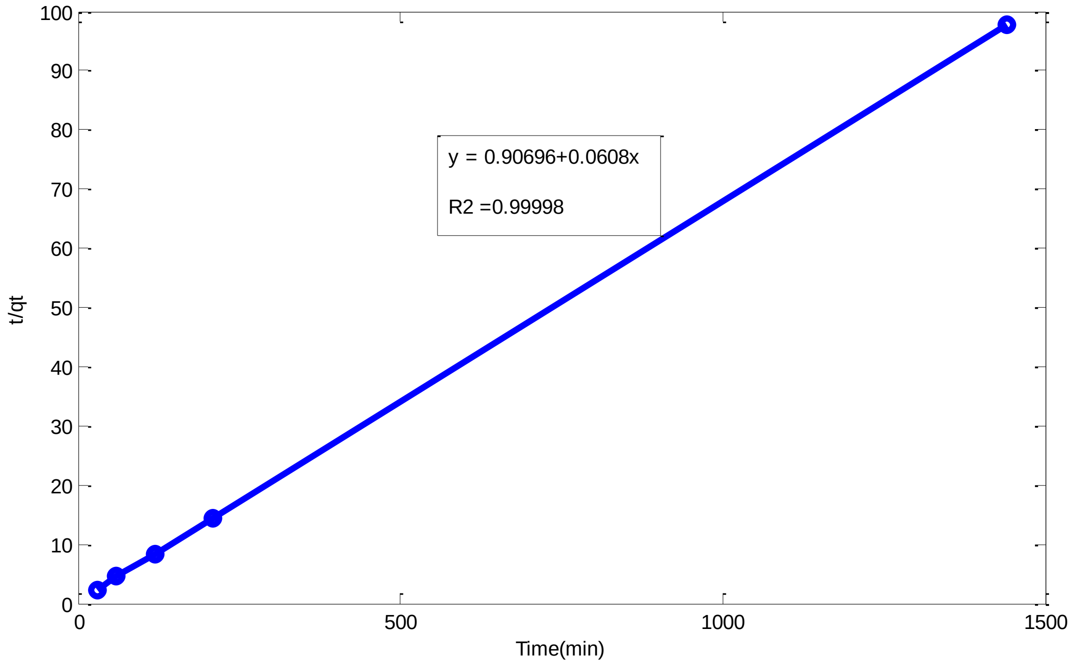

Figure 4.19 Pseudo second order kinetics curve for 75ppm

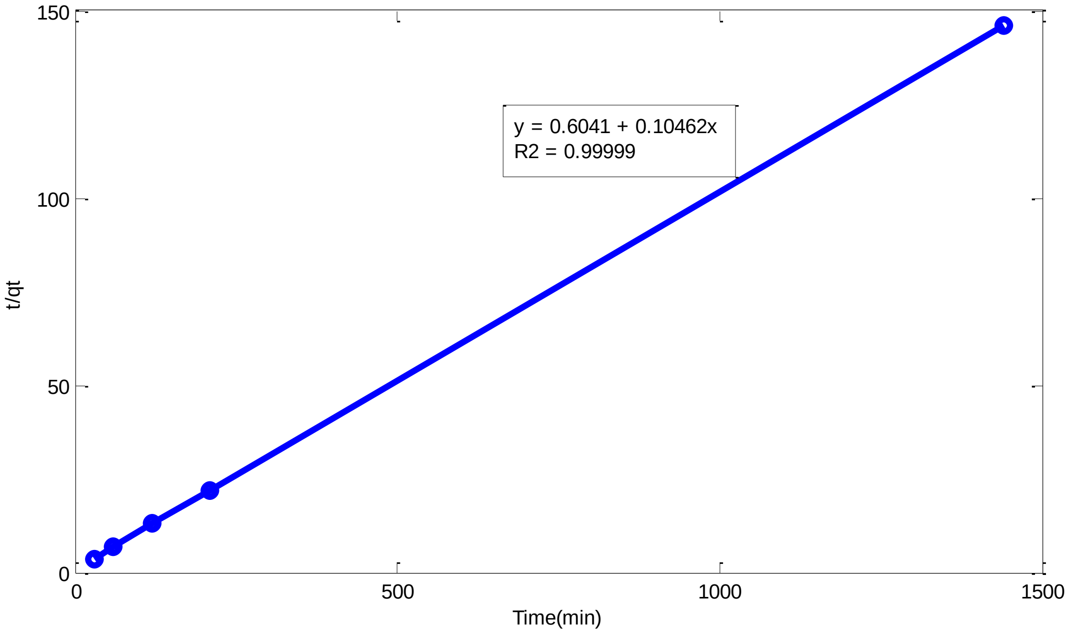

Figure 4.20 Pseudo second order kinetics curve for 50ppm

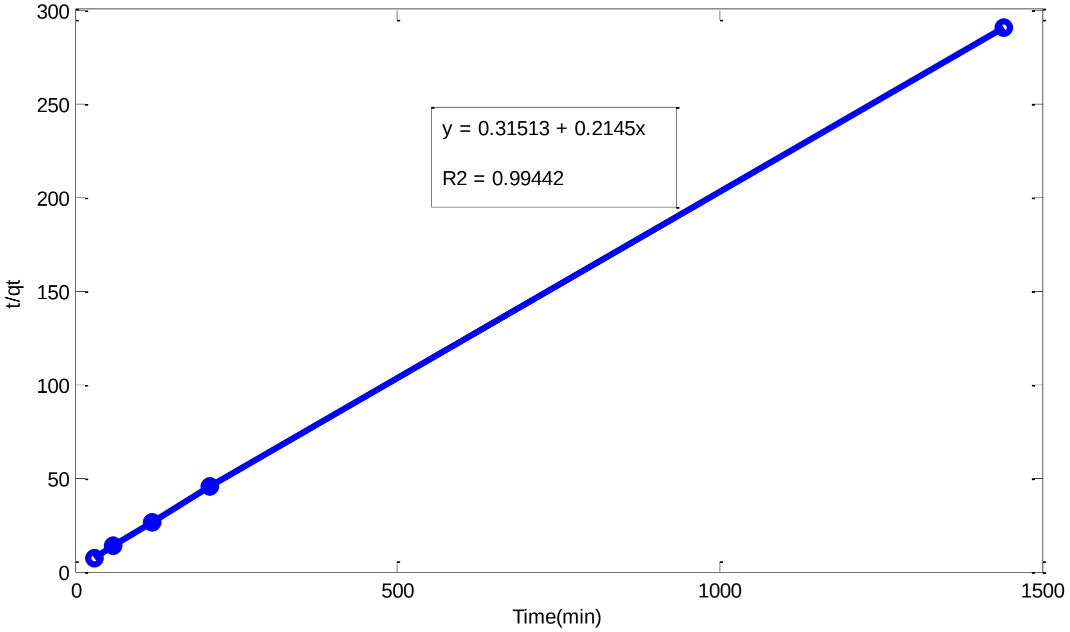

Figure 4.21 Pseudo second order kinetics curve for 25ppm

Table 4.7: Pseudo second order kinetics model data

Time (min)	Initial fluoride concentration (75ppm)		Initial fluoride concentration (50ppm)		Initial fluoride concentration (25ppm)	
	q_t(mg/g)	t/q_t	q_t(mg/g)	t/q_t	q_t(mg/g)	t/q_t
30	13	2.3077	8.12	3.6946	4.37	6.865
60	13.18	4.5524	8.72	6.881	4.4	13.6364
120	14.638	8.1978	9.12	13.1579	4.606	26.053
210	14.7	14.2857	9.64	21.784	4.63	45.3564
1440	14.728	97.773	9.854	146.134	4.956	290.557
4320	14.728	293.319	9.854	438.402	4.956	871.671
Pseudo second order kinetics	75ppm	Intercept ($1/K_2qe^2$)	0.0316			
		K_2	2.151			
		R^2	0.99998			
	50ppm	Intercept ($1/K_2qe^2$)	0.5535			
		K_2	0.1827			
		R^2	0.99999			
	25ppm	Intercept ($1/K_2qe^2$)	3.4929			
		K_2	0.0571			
		R^2	0.9944			

The pseudo-second-order model constants were determined from the slope and intercept of the plot of t/q_t versus t. Contrary to the pseudo-first-order equation, the fitting of the kinetic data in the pseudo-second-order equation showed excellent linearity with high correlation coefficient ($R^2 > 0.99$). So, it was inferred that the adsorption of fluoride onto bone char followed pseudo-second-order kinetics.

The correlation coefficient for pseudo second order kinetics is compared with correlation coefficient of pseudo first order kinetics and the best model that fits the experimental data is selected. The correlation coefficient (R^2) is found to be 0.99998, 0.999992 and 0.994421 for the concentration of 75ppm, 50ppm and 25ppm respectively.

From the given graphs shown above and the parameters in Table 4.6 and Table 4.7, the best kinetic model that fits to the adsorption process is obtained to be pseudo second order kinetics model. Therefore, this model is selected to be the best model for the bone char used.
Hence, taking pseudo second order as best kinetics model, the parameters such as equilibrium mass of adsorption is found to be 14.733, 9.89144 and 5.0163mg/g for the 75ppm ,50ppm and 25ppm concentrations and its rate of adsorption (k_a) values are found to be 2.151, 0.183 and 0.057 g/(mg ·min) respectively.

4.11 Thermodynamic Studies

In order to determine the thermodynamic feasibility of the thermal effects of the sorption, the Gibbs free energy (ΔG°), the entropy ΔS° and the enthalpy (ΔH°) were calculated. The ΔG° is the fundamental criterion to determine if a process occurs spontaneously. For a given temperature, a phenomenon is considered to be spontaneous if the ΔG° has a negative value. Moreover, if ΔH° is positive, the process is endothermic and if it is negative, the process is exothermic. For the determination of ΔH° and ΔS°, the relationship between sorption equilibrium constant K_d and Gibbs free energy was considered at any temperature.

Change in Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o), were evaluated using the following Equations:

$$\ln(K_d) = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} = - \frac{\Delta G°}{RT} \qquad \text{4.7}$$

Where K_d is the equilibrium partition constant calculated as the ratio between adsorption capacity (q_e) and equilibrium concentration (C_e), R is the gas constant (8.314 J/mol/K) and T is the temperature in Kelvin (K). The values of ΔH^o and ΔS^o obtained from the plot of $\ln(K_d)$ vs. 1/T. The plot of $\ln(k_d)$ as a function of 1/T should give a linear relationship with slope of ΔH°/R and an intercept of ΔS°/R. Then ΔG° is obtained at any temperature from the following equation (4.8).

$$\Delta G^\circ = -RT \ln(K_d) \quad \text{……} 4.8$$

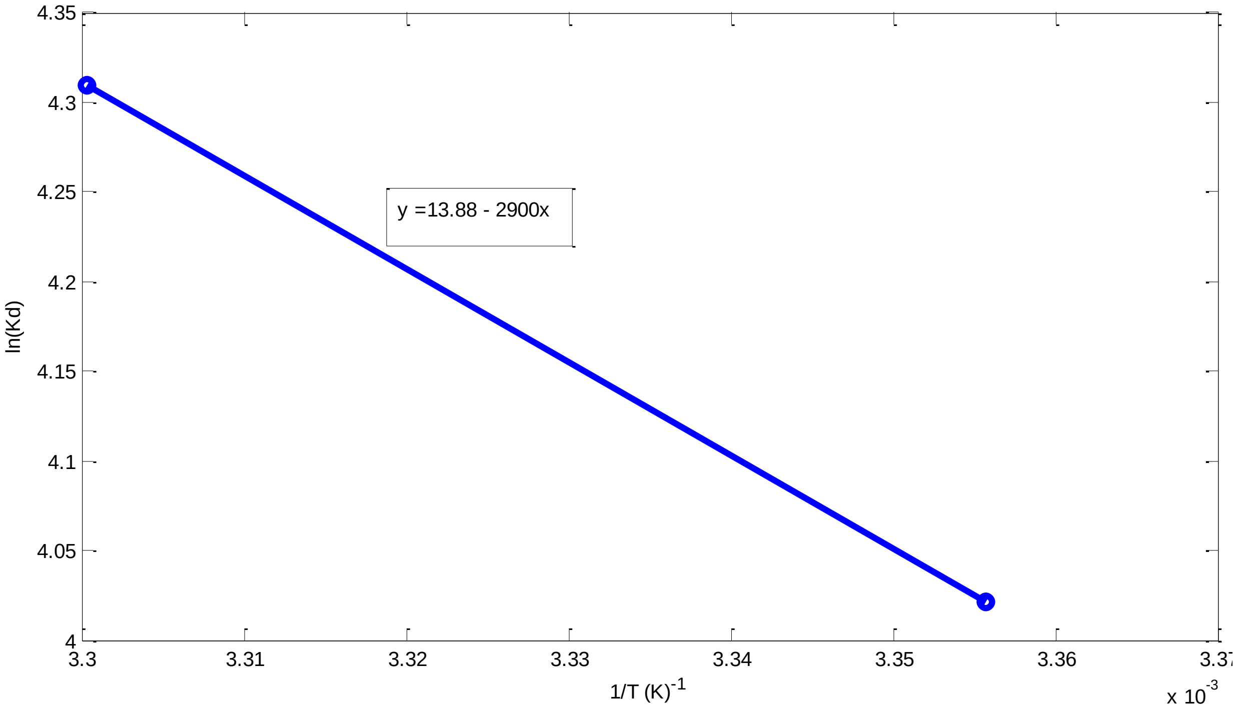

Figure 4.22 Thermodynamics of the adsorption of fluoride onto bone char

The positive ΔHº value indicates the endothermic nature of the process. Moreover, the positive ΔSº value corresponds to an increase in the degree of freedom of the adsorbed species. The negative ΔGº value confirmed the reaction feasibility and the spontaneity of the adsorption process. Further, the large absolute value for ΔGº obtained in this study indicates that chemical adsorption is the predominant mechanism in the sorption process. But, ΔGº was positive at 288K indicating that the reaction is not spontaneous at lower temperatures (below 293K).

It is clear from Table 4.8 that bone char have large capacity in the removal of fluoride ions from aqueous solutions.

Table 4.8 Thermodynamic parameters for adsorption of fluoride onto bone char

T(K)	ΔG^o(KJ/mole)	ΔS^o(J/(mole.K))	ΔH^o(KJ/mole)
288	3.75	115.4	24.11
293	-9.57		
298	-9.96		
303	-10.86		
308	-10.27		

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the results of this work, it is concluded that bone can be used as raw material for the production of bone char adsorbent for fluoride removal. One of the novelties of this work is the optimization of the process parameters namely, temperature, residence time and nitrogen gas pressure during charcoal preparation. Results obtained from this study showed that, the pyrolysis temperature has major effect in the removal efficiency of bone char. As the temperature increased from 400℃ to 500℃ the percentage removal also increased. Beyond temperature of 500℃, percentage removal decreased. Since the organic components of bone add color and taste to drinking water it is better to heat until all organic components converted into inorganic matter. Hence it is better to use 500℃ in order to avoid color and taste effect with 99% removal of fluoride.

Generally, the residence time has the same effect as temperature for the removal of fluoride. When the residence time increased, the amount of fluoride removal increased up to the maximum removal condition attained. This is due to increase in the exposure to heat of the bone either increasing temperature or increasing residence time up to the optimum condition result in better removal. Beyond the maximum removal increasing either temperature or residence time decreased the percentage removal of fluoride.

The result from this study also indicated that inlet nitrogen gas has insignificant effect on fluoride removal. The inlet nitrogen pressure gave slightly better fluoride removal effect at 2.5bar which was 99.958% than at 1.5bar which was 99.83 at constant temperature of 500℃ and time of 90 minutes.

The experimental parameters such as pH, initial concentration, adsorbent dose, contact time and temperature were investigated for their potential impact on bone char uptake capacity for fluoride. The results indicated that increase in adsorption with increase in initial concentration, adsorbent dose and contact time. The pH and temperature have indicated better adsorption efficiency at 7 and 30℃ respectively. But it is insignificant when compared to other points.

Furthermore, when considering the adsorption isotherm, bone char was studied and fitted to both Langmuir and Freundlich isotherms. The fluoride adsorption was found to be best fitted with the Freundlich isotherm better than the Langmuir isotherm and the equilibrium time was found to be around 24 hours.

The adsorption kinetics was also determined and the kinetic results obtained from this study fitted well with the pseudo second order kinetic model. The increase in surface area and volume of the bone char enhanced the adsorption efficiency of the bone after being treated in varying temperature, nitrogen and time.

Therefore, bone charcoal can be used efficiently and effectively for fluoride removal from drinking water and waste water with appropriate selection of synthesis conditions for bone char preparation processes. According to this study it is concluded that optimum conditions were 500℃, 60 minutes and 1.5bar nitrogen.

5.2 Recommendation

Bone char has several industrial applications depending on its porous structure and adsorption capacity. To increase the adsorptive efficiency of the char produced from cattle bone, it is recommended to carry out experiments with different experimental parameters. Some of the most critical parameters are the heating rate, pyrolysis temperature, inlet nitrogen pressure and holding time.

The future efforts in this field should include the investigation of the effect of activating agents. To get more information on the characteristics of the product, it is better to perform the BET tests in order to analyze the surface area and volume of the pores produced.

Natural water may contain many an ions that compete with fluoride for adsorption such as HCO_3^-, SO_4^{2-}, and Cl^- [37]. The effect of other ions should be investigated so that it helps to selectively use the sorbent in preference to other ions.

The design of appropriate equipment is required from future studies.

There are many regions in Ethiopia affected by naturally fluoridated water. People live in those regions exposed to fluorosis which is dangerous level of fluoride problem. It is advisable to conduct research to scale up this research for solving community problem. National Tobacco Enterprise S.C has farm near to Hawassa and its workers are endangered by this problem. The cost for health care due to such problem and absence from work is significant. Both industries and universities have responsibility to participate in the community problem solving. Hence the problem can be solved by collaboration with such industries like National Tobacco Enterprise S.C.

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APPENDICES

Appendix A: Bar graph representations of the conditions of bone char preparation

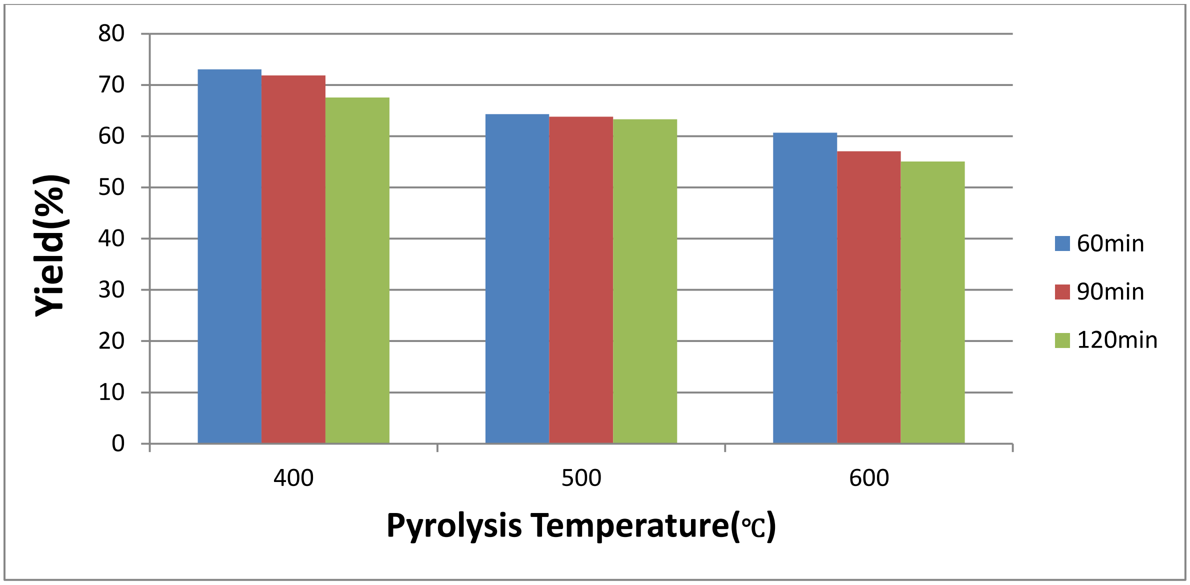


Figure A1. Effect of temperature and time on yield at 2bar

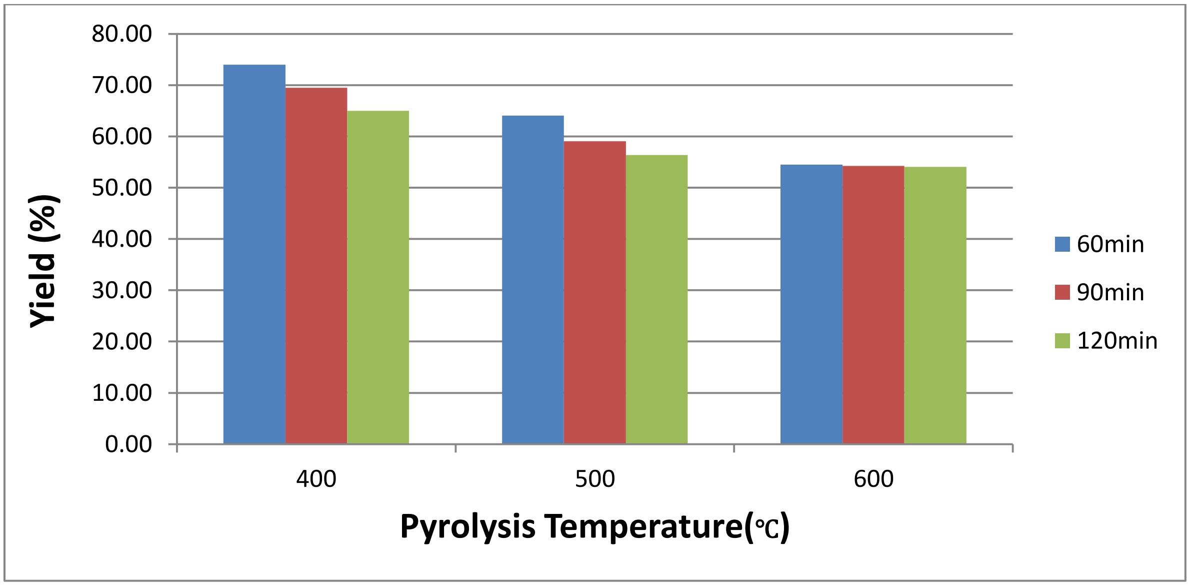


Figure A2. Effect of temperature and time on yield at 2.5bar

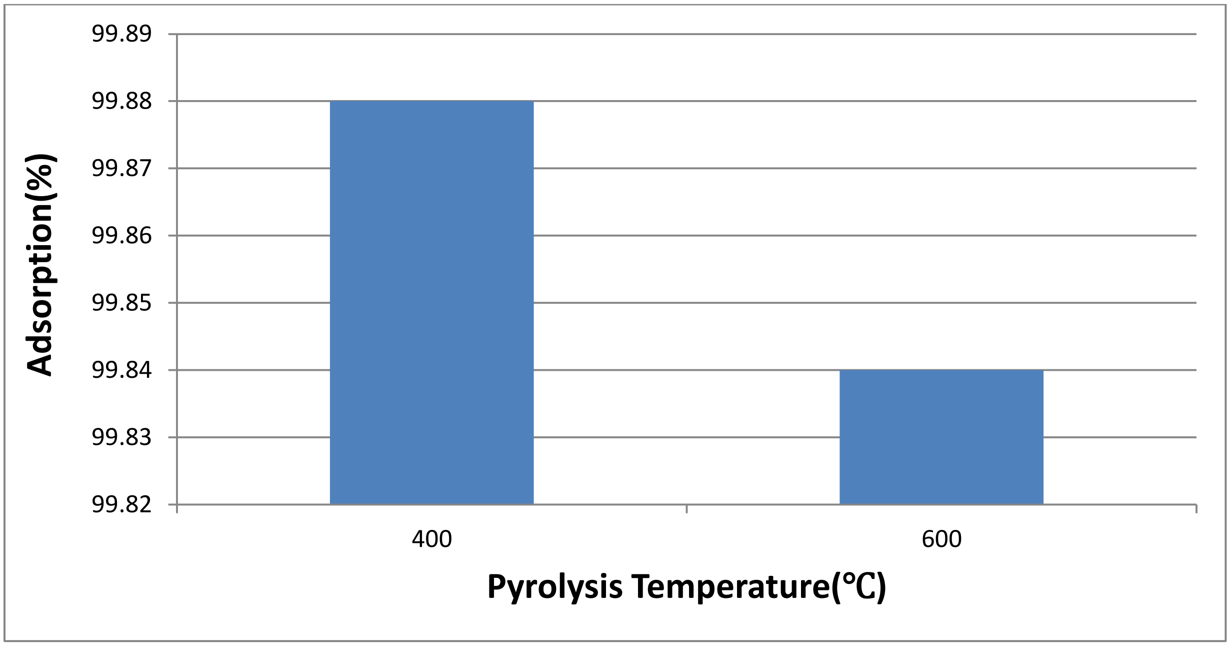


Figure A3. Effect of temperature on adsorption at 1.5bar and 60minutes

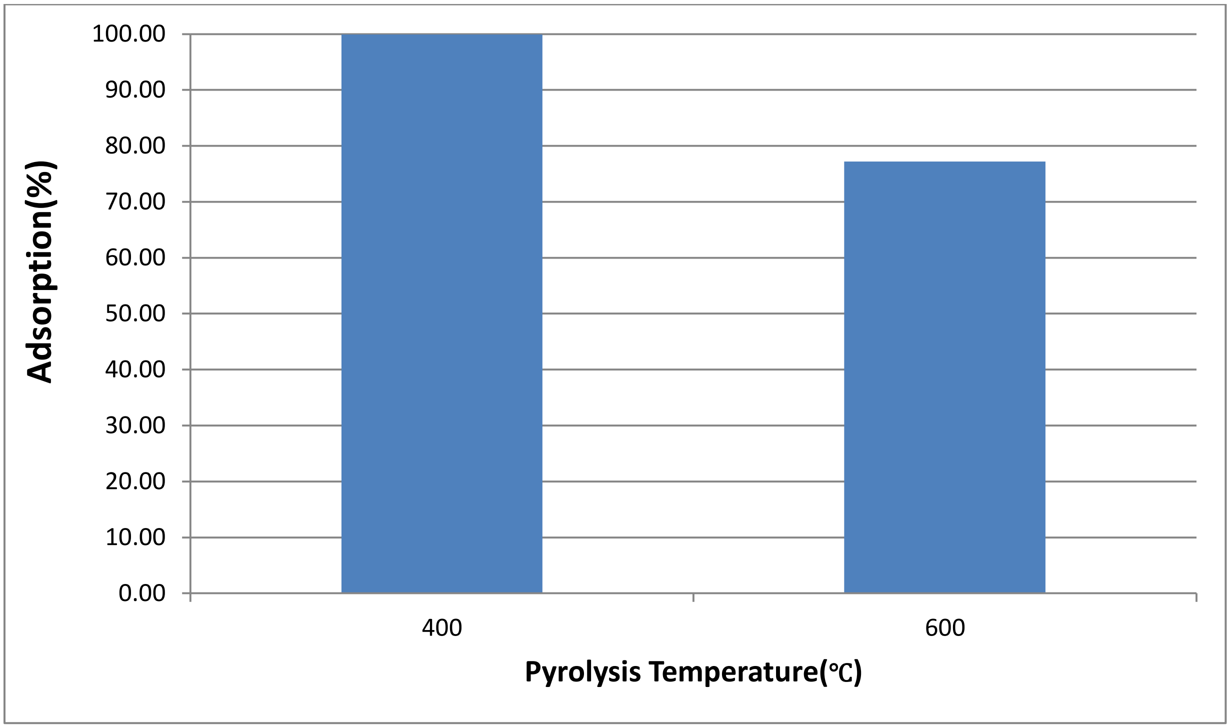


Figure A4. Effect of temperature on adsorption at 1.5bar and 120minutes

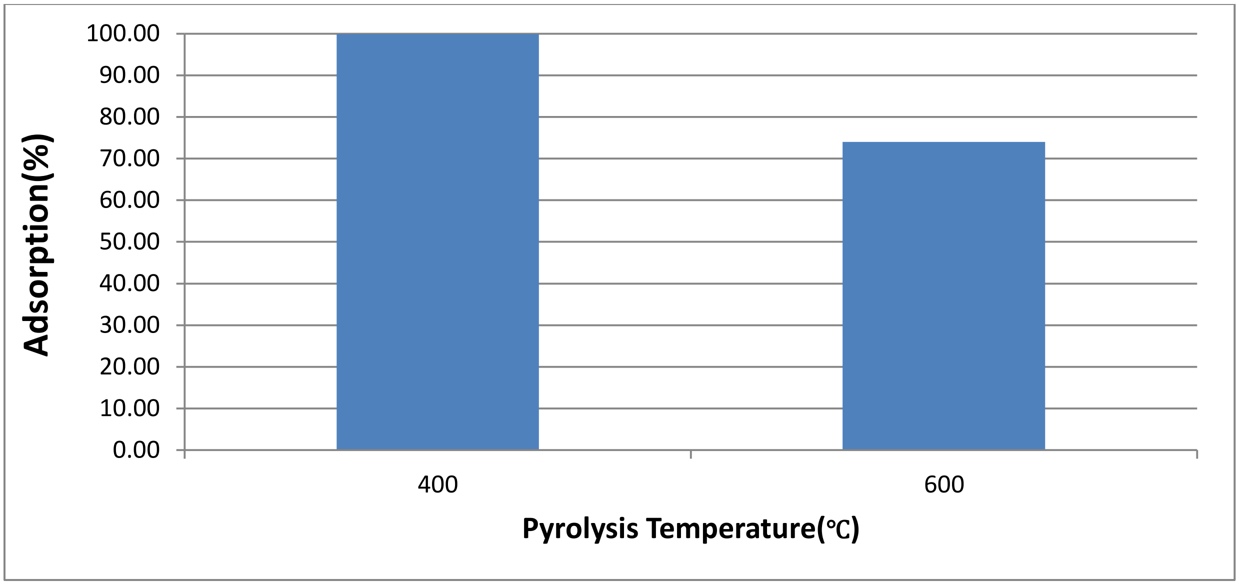


Figure A5. Effect of temperature on adsorption at 2.5bar and 60minutes

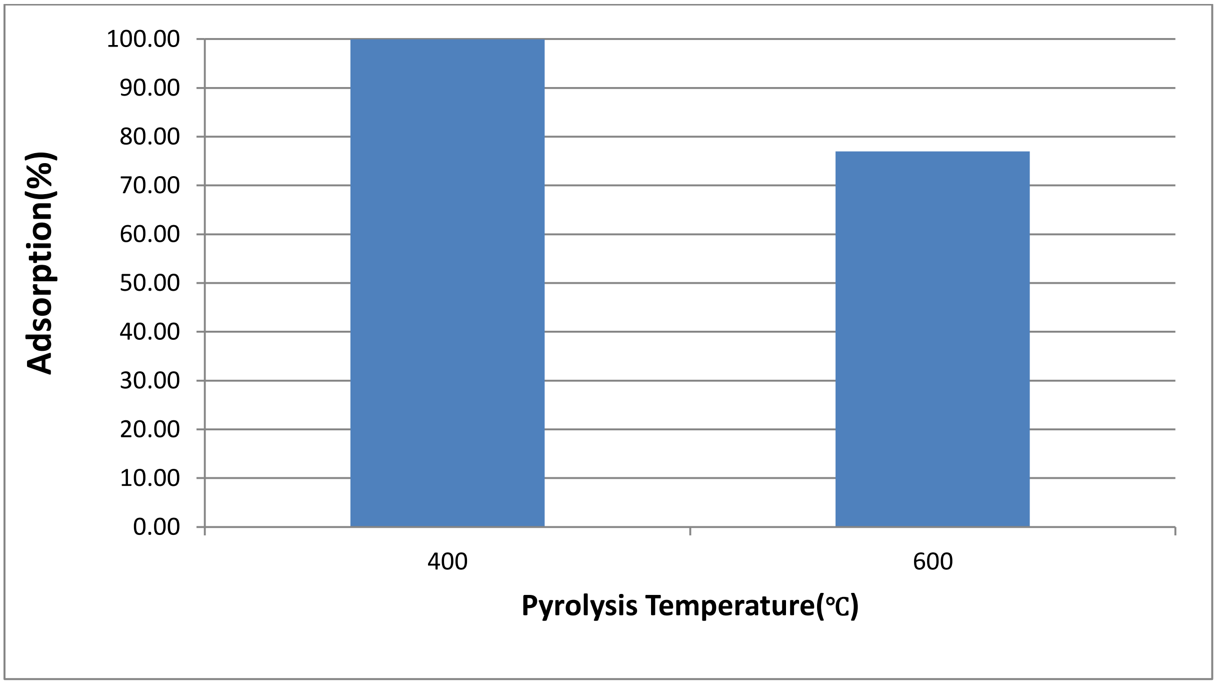


Figure A6. Effect of temperature on adsorption at 2.5bar and 120minutes

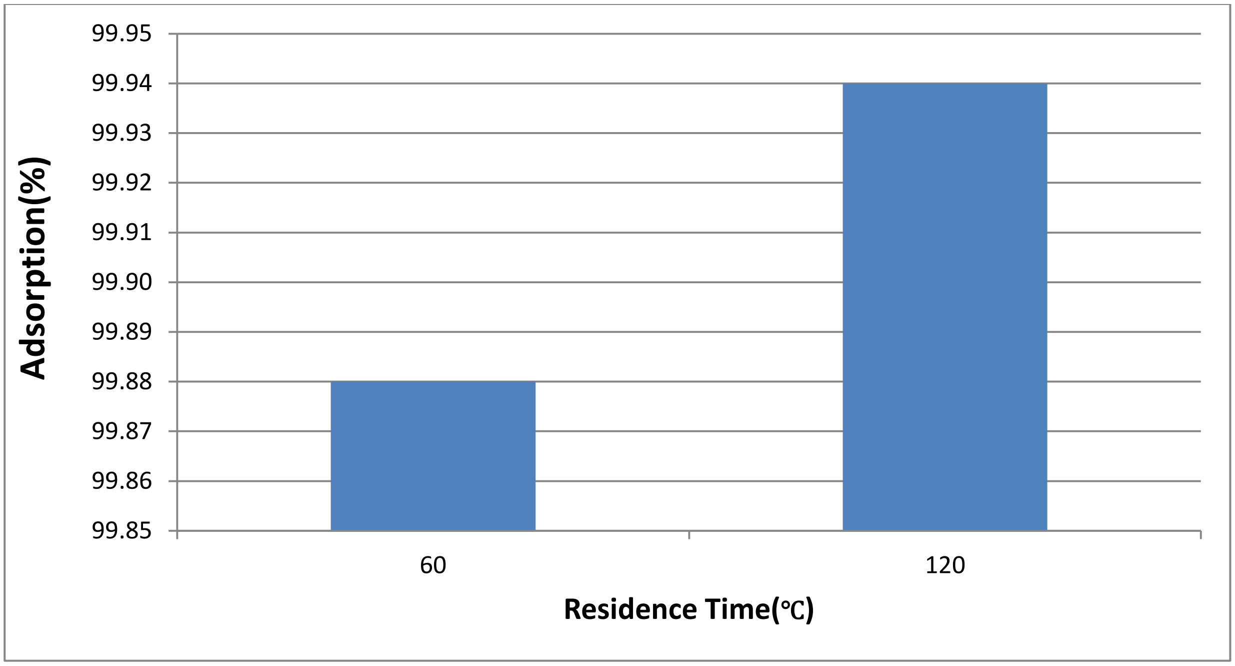


Figure A7. Effect of residence time on adsorption at 1.5bar and 400℃

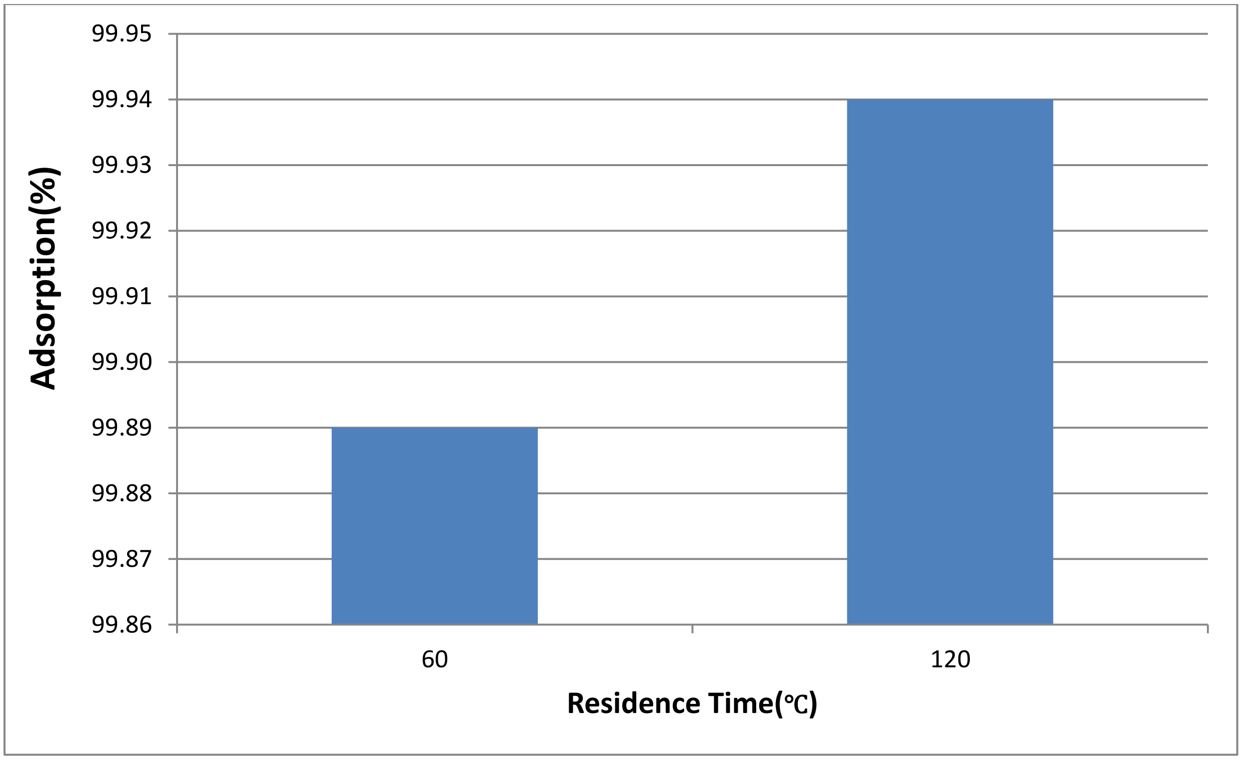


Figure A8. Effect of residence time on adsorption at 2.5bar and 400℃

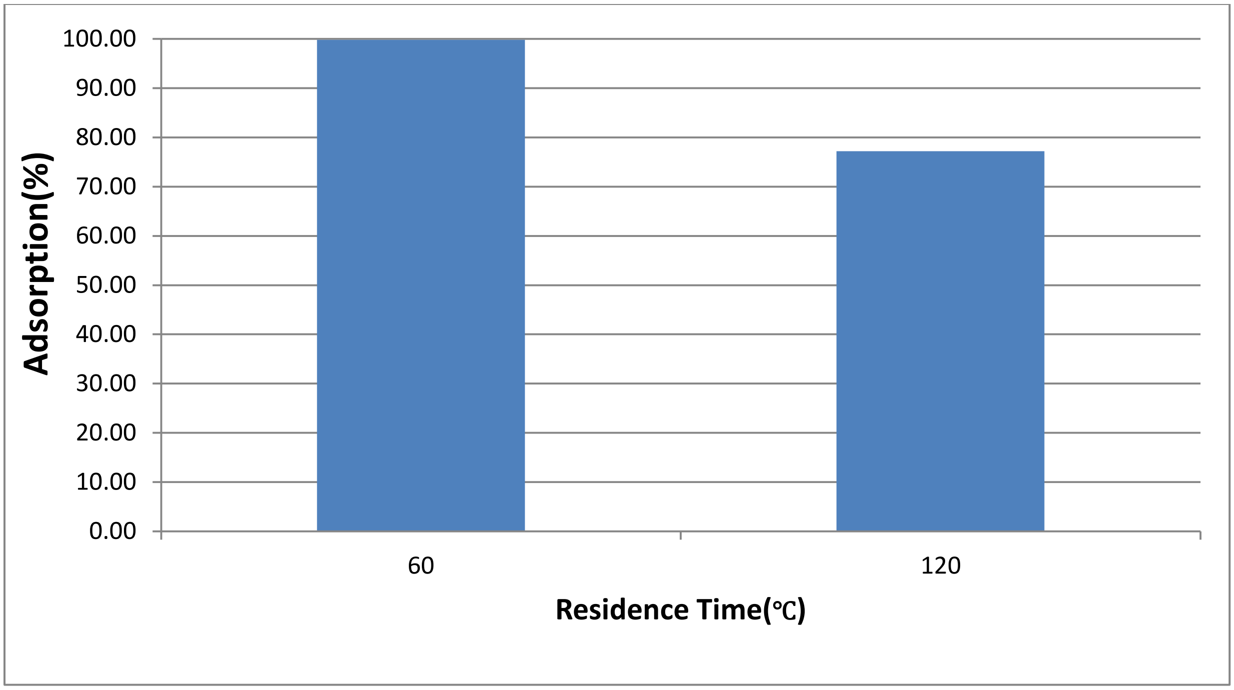


Figure A9. Effect of residence time on adsorption at 1.5bar and 600℃

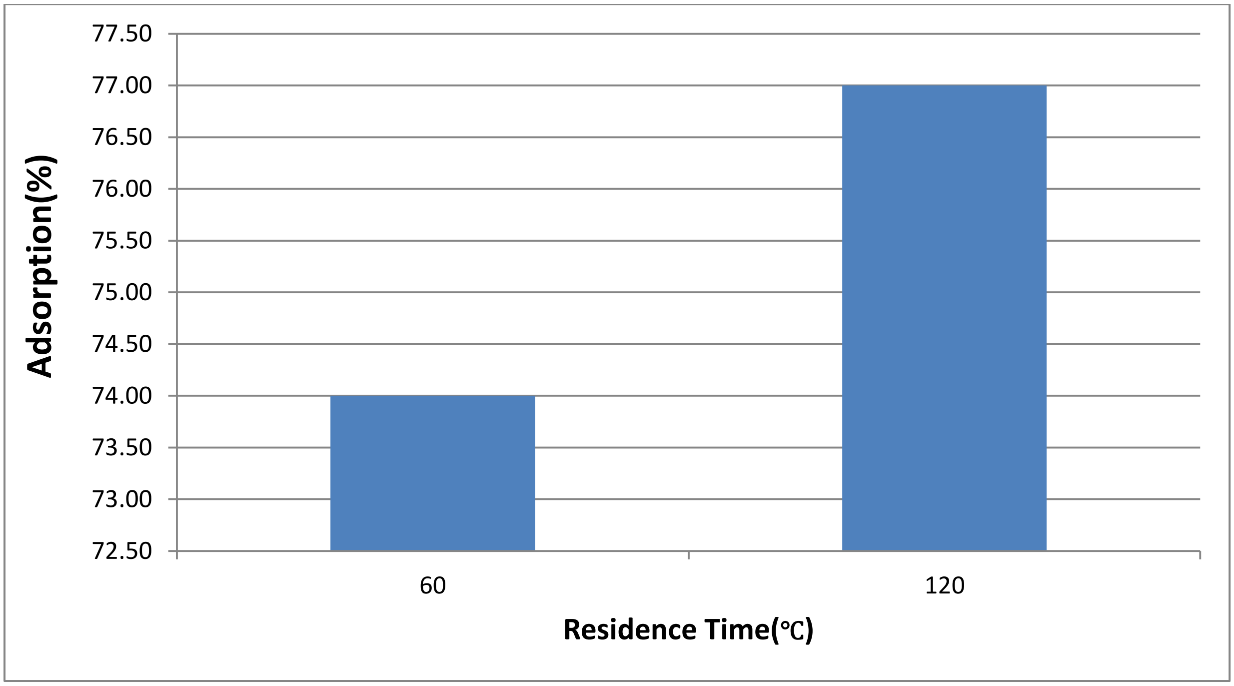


Figure A10. Effect of residence time on adsorption at 2.5bar and 600℃

Appendix B ANOVA results for yield and adsorption

Response1(**yield**)

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob >F**	
Model	550.26	9	61.14	23.64	< 0.0001	significant
A-temperture	*417.07*	*1*	*417.07*	*161.28*	*< 0.0001*	
B-Inlet N2 pressure	*3.26*	*1*	*3.26*	*1.26*	*0.2881*	
C-time	*58.30*	*1*	*58.30*	*22.54*	*0.0008*	
AB15.11	*1*	*15.11*	*5.84*	*0.0363*		
AC17.28	*1*	*17.28*	*6.68*	*0.0272*		
BC2.28	*1*	*2.28*	*0.88*	*0.3696*		
A^2*2.52*	*1*	*2.52*	*0.98*	*0.3466*		
B^2*30.34*	*1*	*30.34*	*11.73*	*0.0065*		
C^2*0.23*	*1*	*0.23*	*0.090*	*0.7705*		
Residual	25.86	10	2.59			
Lack of Fit	*20.48*	*5*	*4.10*	*3.81*	*0.0843*	*not significant*
Pure Error	*5.38*	*5*	*1.08*			
Cor Total	576.12	19				

The Model F-value of 23.64 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, C, AB, AC, B^2 are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The "Lack of Fit F-value" of 3.81 implies there is a 8.43% chance that a "Lack of Fit F-value" this large could occur due to noise. Lack of fit is bad -- we want the model to fit. This relatively low probabiity (<10%) is troubling.

Std. Dev.	1.61	R-Squared	0.9551
Mean	63.19	Adj R-Squared	0.9147
C.V. %	2.55	Pred R-Squared	0.6442
PRESS	205.00	Adeq Precision	17.083

The "Pred R-Squared" of 0.6442 is not as close to the "Adj R-Squared" of 0.9147 as one might normally expect. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider are model reduction, response tranformation, outliers, etc.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 17.083 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	64.22	1	0.55	62.99	65.45	
A-temperture	-6.46	1	0.51	-7.59	-5.33	1.00
B-Inlet N2 pressure	-0.57	1	0.51	-1.70	0.56	1.00
C-time	-2.41	1	0.51	-3.55	-1.28	1.00
AB-1.37	1	0.57	-2.64	-0.11	1.00	
AC1.47	1	0.57	0.20	2.74	1.00	
BC0.53	1	0.57	-0.73	1.80	1.00	
$A^2$0.96	1	0.97	-1.20	3.12	1.82	
B^2-3.32	1	0.97	-5.48	-1.16	1.82	
$C^2$0.29	1	0.97	-1.87	2.45	1.82	

Final Equation in Terms of Coded Factors:

yield = +64.22 -6.46* A -0.57* B -2.41* C -1.37* A * B +1.47* A * C +0.53* B * C +0.96* A^2 -3.32* B^2+0.29 * C^2

Final Equation in Terms of Actual Factors:

yield = +80.42195 -0.14948 * temperture +62.54366* Inlet N2 pressure -0.45478* time -0.027482 * temperture * Inlet N2 pressure +4.89875E-004* temperture * time +0.035608* Inlet N2 pressure * time +9.57727E-005* temperture^2 -13.28709* Inlet N2 pressure^2 +3.23030E-004* time^2

Response2(Adsorption)

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	1930.40	9	214.49	11.26	0.0004 significant
A-temperture	*1043.46*	*1*	*1043.46*	*54.76*	*< 0.0001*
B-inlet N pressure	*67.08*	*1*	*67.08*	*3.52*	*0.0901*
C-time	*38.30*	*1*	*38.30*	*2.01*	*0.1866*
AB84.77	*1*	*84.77*	*4.45*	*0.0611*	
AC48.71	*1*	*48.71*	*2.56*	*0.1409*	
BC82.12	*1*	*82.12*	*4.31*	*0.0646*	
$A^2$460.34	*1*	*460.34*	*24.16*	*0.0006*	
$B^2$14.28	*1*	*14.28*	*0.75*	*0.4069*	
$C^2$14.37	*1*	*14.37*	*0.75*	*0.4054*	
Residual	190.54	10	19.05		
Lack of Fit	*190.53*	*5*	*38.11*	*82577.91*	*< 0.0001 significant*
Pure Error	*2.307E-003*	*5*	*4.615E-004*		
Cor Total	2120.94	19			

The Model F-value of 11.26 implies the model is significant. There is only a 0.04% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, A^2 are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The "Lack of Fit F-value" of 82577.91 implies the Lack of Fit is significant. There is only a 0.01% chance that a "Lack of Fit F-value" this large could occur due to noise.
Significant lack of fit is bad -- we want the model to fit.

Std. Dev.	4.37	R-Squared	0.9102
Mean	94.80	Adj R-Squared	0.8293
C.V. %	4.60	Pred R-Squared	-0.2732
PRESS	2700.28	Adeq Precision	10.327

A negative "Pred R-Squared" implies that the overall mean is a better predictor of your response than the current model.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 10.327 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	98.99	1	1.50	95.64	102.33	
A-temperture	-10.21	1	1.38	-13.29	-7.14	1.00
B-inlet N pressure	-2.59	1	1.38	-5.67	0.49	1.00
C-time	-1.96	1	1.38	-5.03	1.12	1.00
AB-3.26	1	1.54	-6.69	0.18	1.00	
AC-2.47	1	1.54	-5.91	0.97	1.00	
BC3.20	1	1.54	-0.23	6.64	1.00	
A^2-12.94	1	2.63	-18.80	-7.07	1.82	
$B^2$2.28	1	2.63	-3.59	8.14	1.82	
$C^2$2.29	1	2.63	-3.58	8.15	1.82	

Final Equation in Terms of Coded Factors:

Adsorption = +98.99 -10.21 * A -2.59 * B -1.96 * C -3.26 * A * B -2.47* A * C+3.20 * B * C -12.94 * A^2 +2.28 * B^2 +2.29 * C^2

Final Equation in Terms of Actual Factors:

Adsorption = -163.79239 +1.39590 * temperture -28.31309* inlet N_2 pressure -0.53841 * time -0.065103 * temperture * inlet N_2 pressure -8.22542E-004 * temperture * time +0.21359 * inlet N_2 pressure * time -1.29382E-003* temperture^2 +9.11527* inlet N_2 pressure^2 +2.54035E-003* time^2

Appendix C: Graphical representation of response factors relationship as obtained from design expert 7.0 program

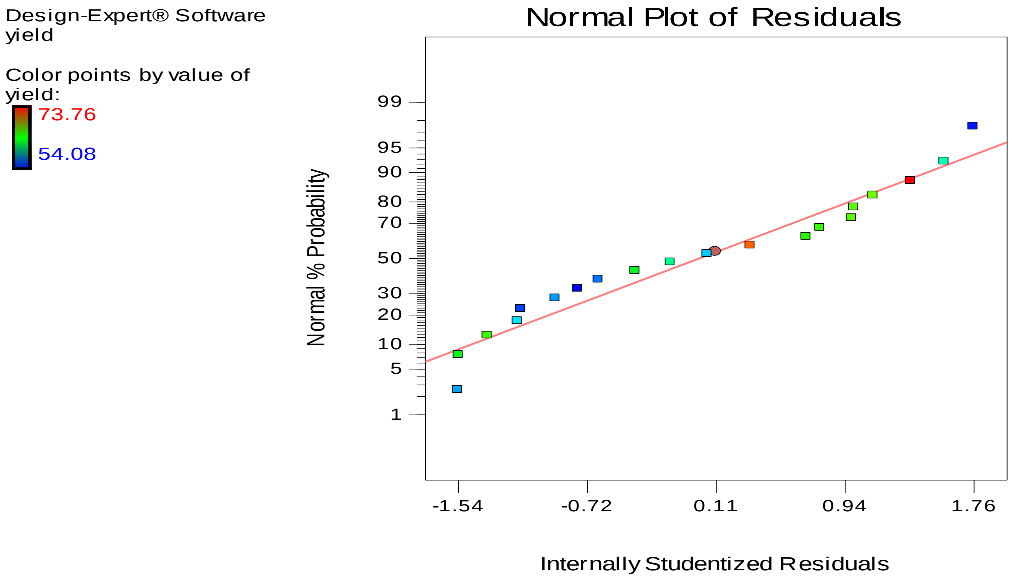


Figure A11. Normal % probability against internally studentized residuals for yield and adsorption

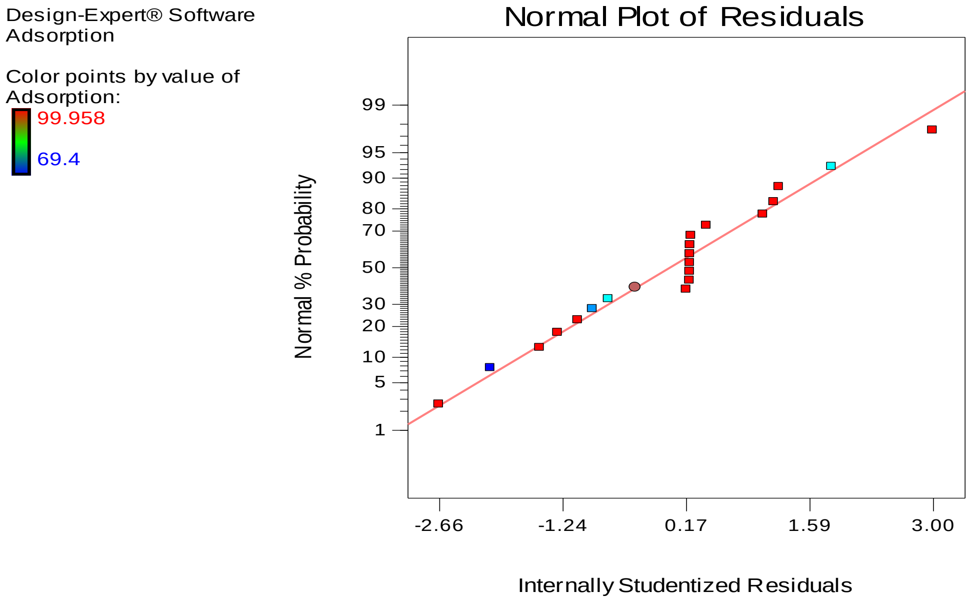


Figure A12. Normal % probability against internally studentized residuals for yield and adsorption.

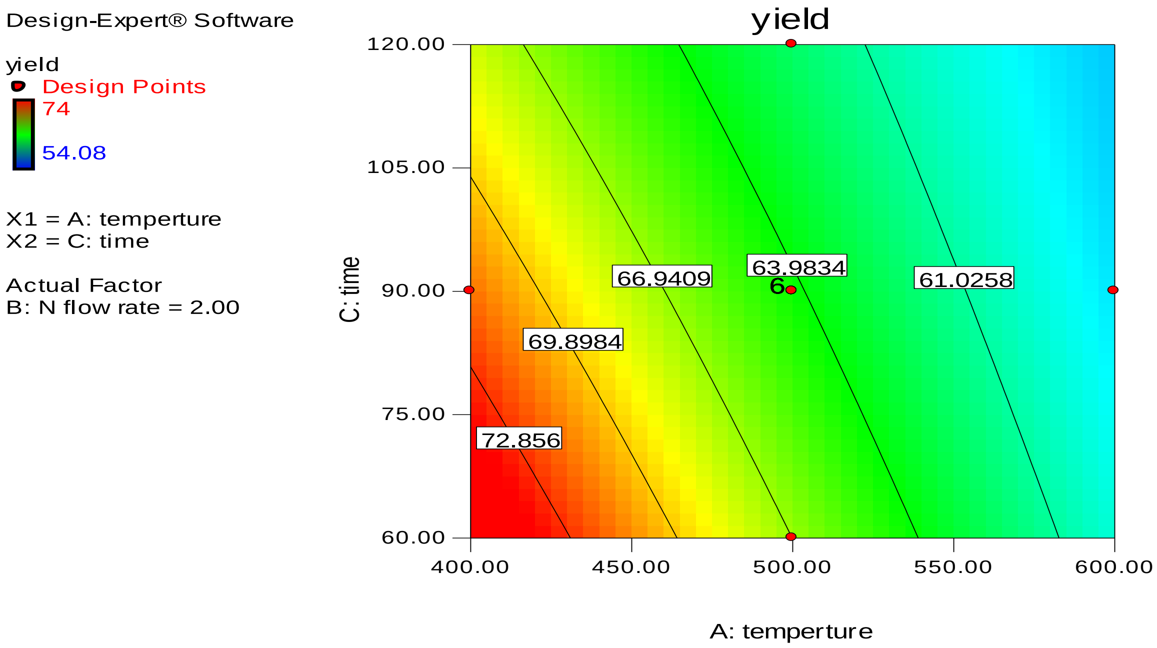


Figure A13. Yield against time and temperature

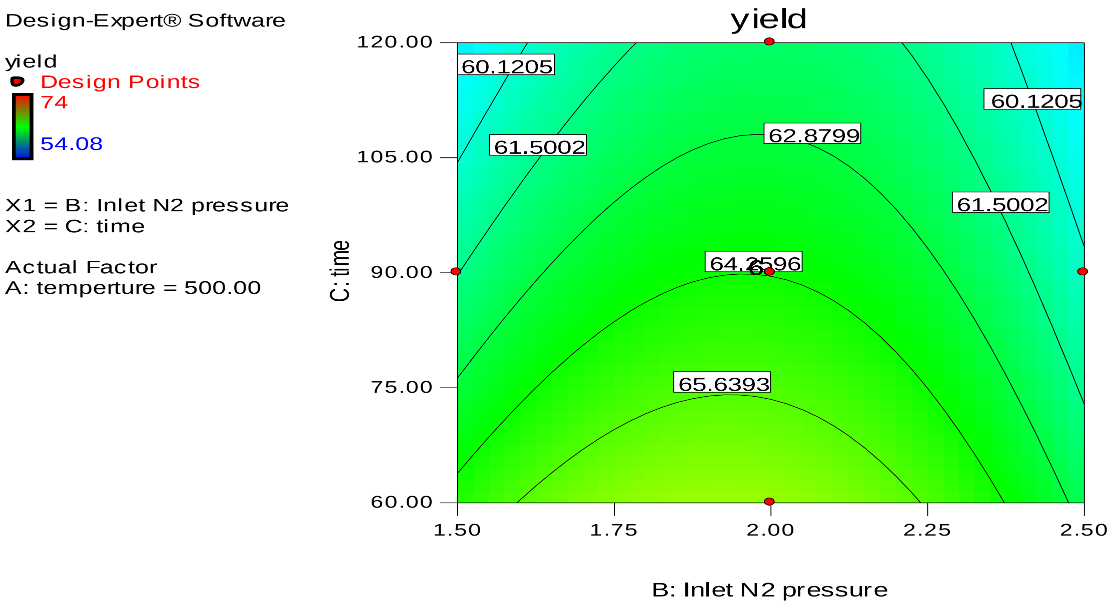


Figure A14. Yield against time and inlet N_2 pressure

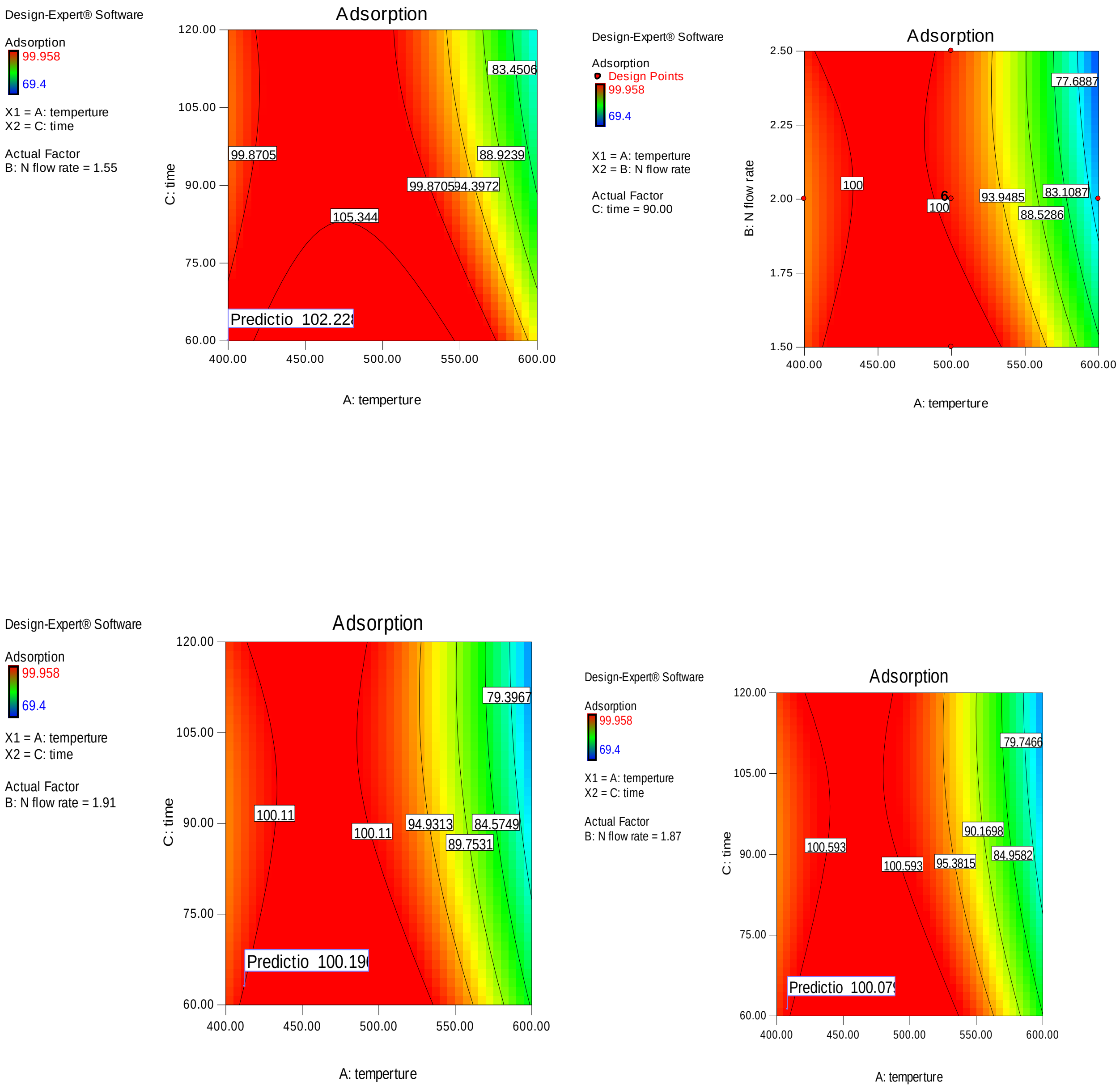


Figure A15. Optimum adsorption region with contour

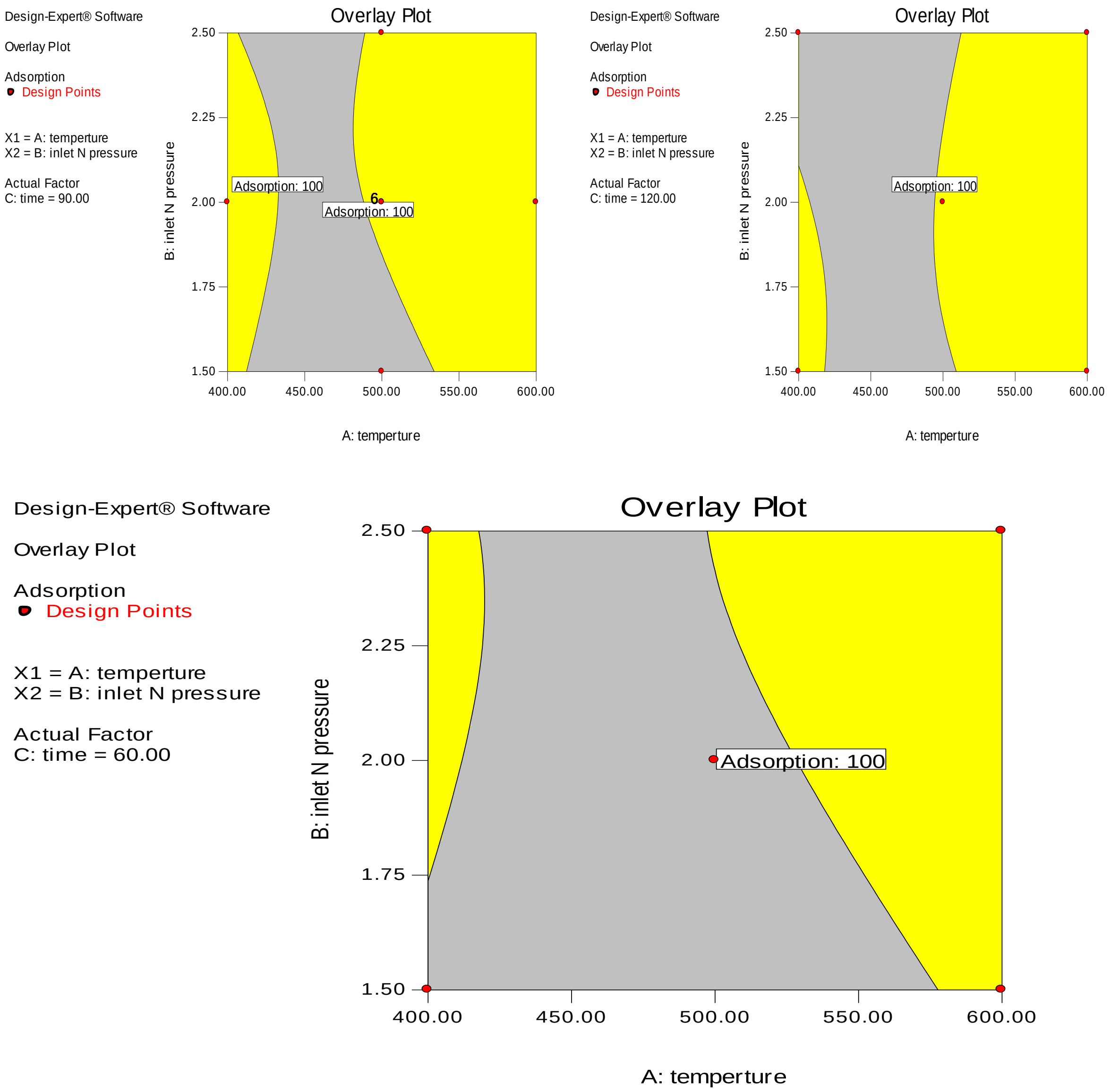
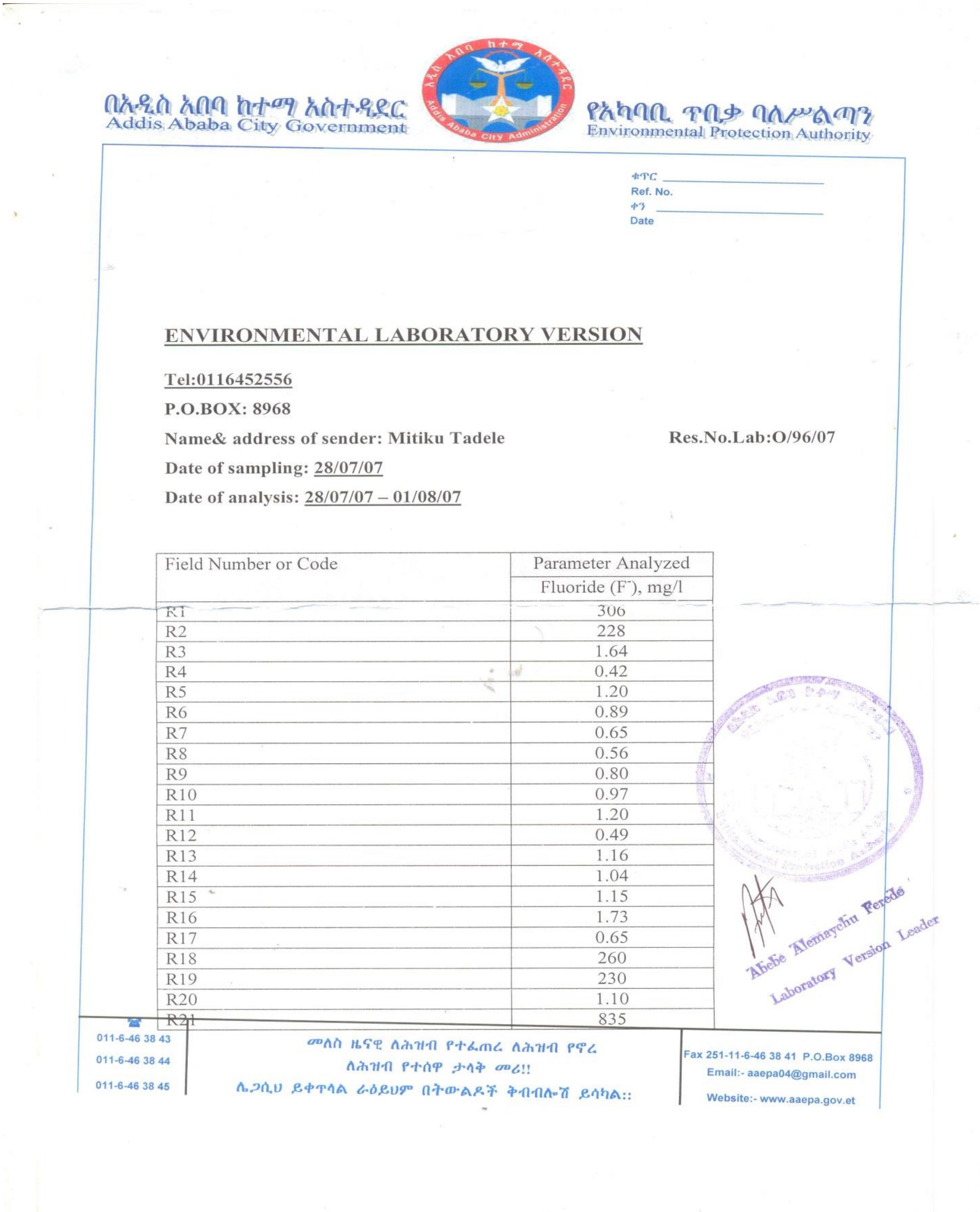


Figure A16. Maximum adsorption region shaded with gray

Appendix D Adsorption result as obtained from Addis Ababa EPA



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Addis Ababa City Government

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Environmental Protection Authority

ቁጥር ____________
Ref. No.
ቀን ____________
Date

ENVIRONMENTAL LABORATORY VERSION

Tel:0116452556

P.O.BOX: 8968

Name& address of sender: Mitiku Tadele

Res.No.Lab:O/96/07

Date of sampling: 28/07/07

Date of analysis: 28/07/07 – 01/08/07

Field Number or Code	Parameter Analyzed
	Fluoride (F^-), mg/l
R1	306
R2	228
R3	1.64
R4	0.42
R5	1.20
R6	0.89
R7	0.65
R8	0.56
R9	0.80
R10	0.97
R11	1.20
R12	0.49
R13	1.16
R14	1.04
R15	1.15
R16	1.73
R17	0.65
R18	260
R19	230
R20	1.10
R21	835

Abebe Alemayehu Ferede
Laboratory Version Leader

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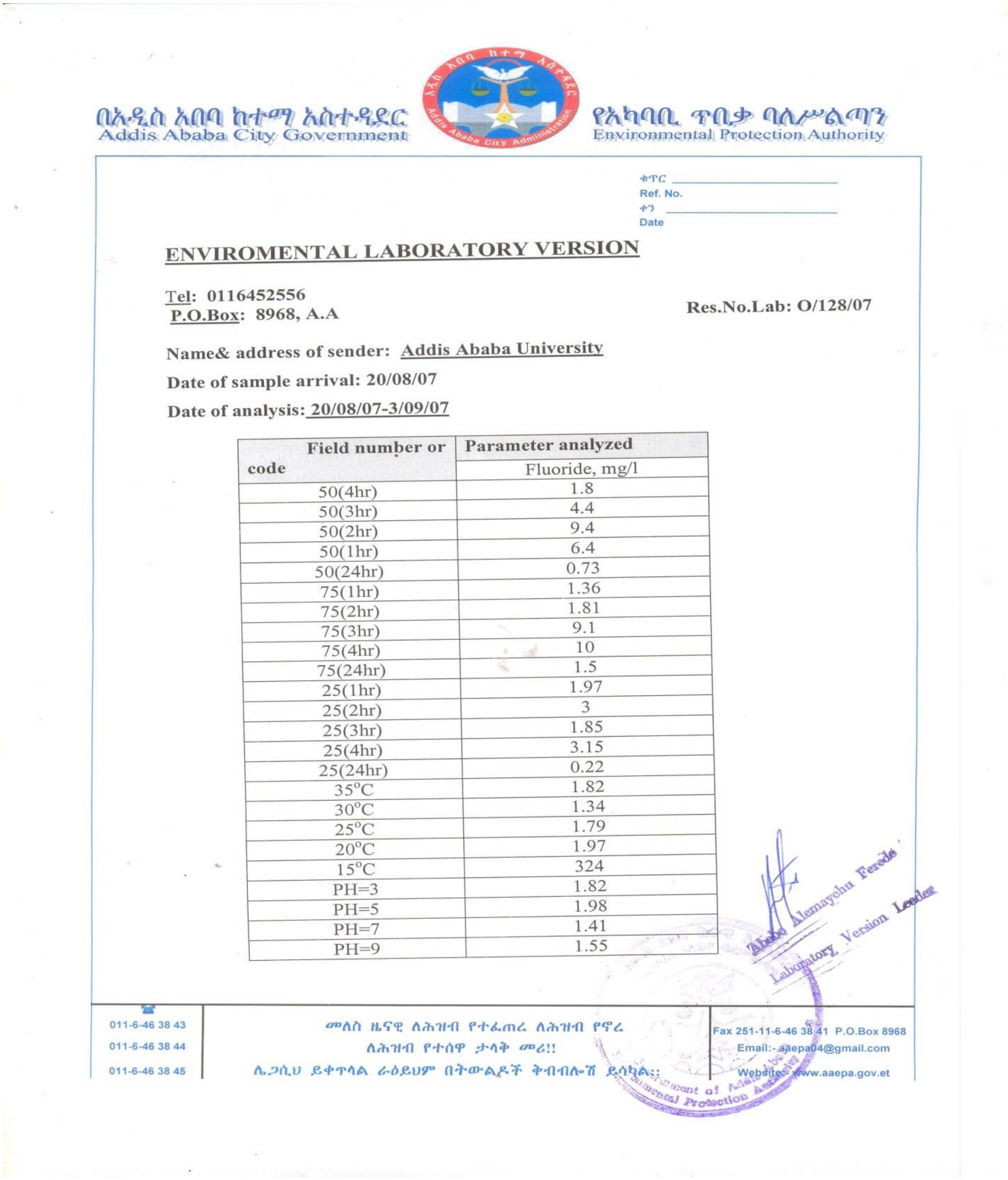
Fax 251-11-6-46 38 41 P.O.Box 8968
Email:- aaepa04@gmail.com
Website:- www.aaepa.gov.et



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Environmental Protection Authority

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ቀን ______________
Date

ENVIROMENTAL LABORATORY VERSION

Tel: 0116452556
P.O.Box: 8968, A.A

Res.No.Lab: O/128/07

Name& address of sender: Addis Ababa University

Date of sample arrival: 20/08/07

Date of analysis: 20/08/07-3/09/07

Field number or code	Parameter analyzed
	Fluoride, mg/l
50(4hr)	1.8
50(3hr)	4.4
50(2hr)	9.4
50(1hr)	6.4
50(24hr)	0.73
75(1hr)	1.36
75(2hr)	1.81
75(3hr)	9.1
75(4hr)	10
75(24hr)	1.5
25(1hr)	1.97
25(2hr)	3
25(3hr)	1.85
25(4hr)	3.15
25(24hr)	0.22
35°C	1.82
30°C	1.34
25°C	1.79
20°C	1.97
15°C	324
PH=3	1.82
PH=5	1.98
PH=7	1.41
PH=9	1.55

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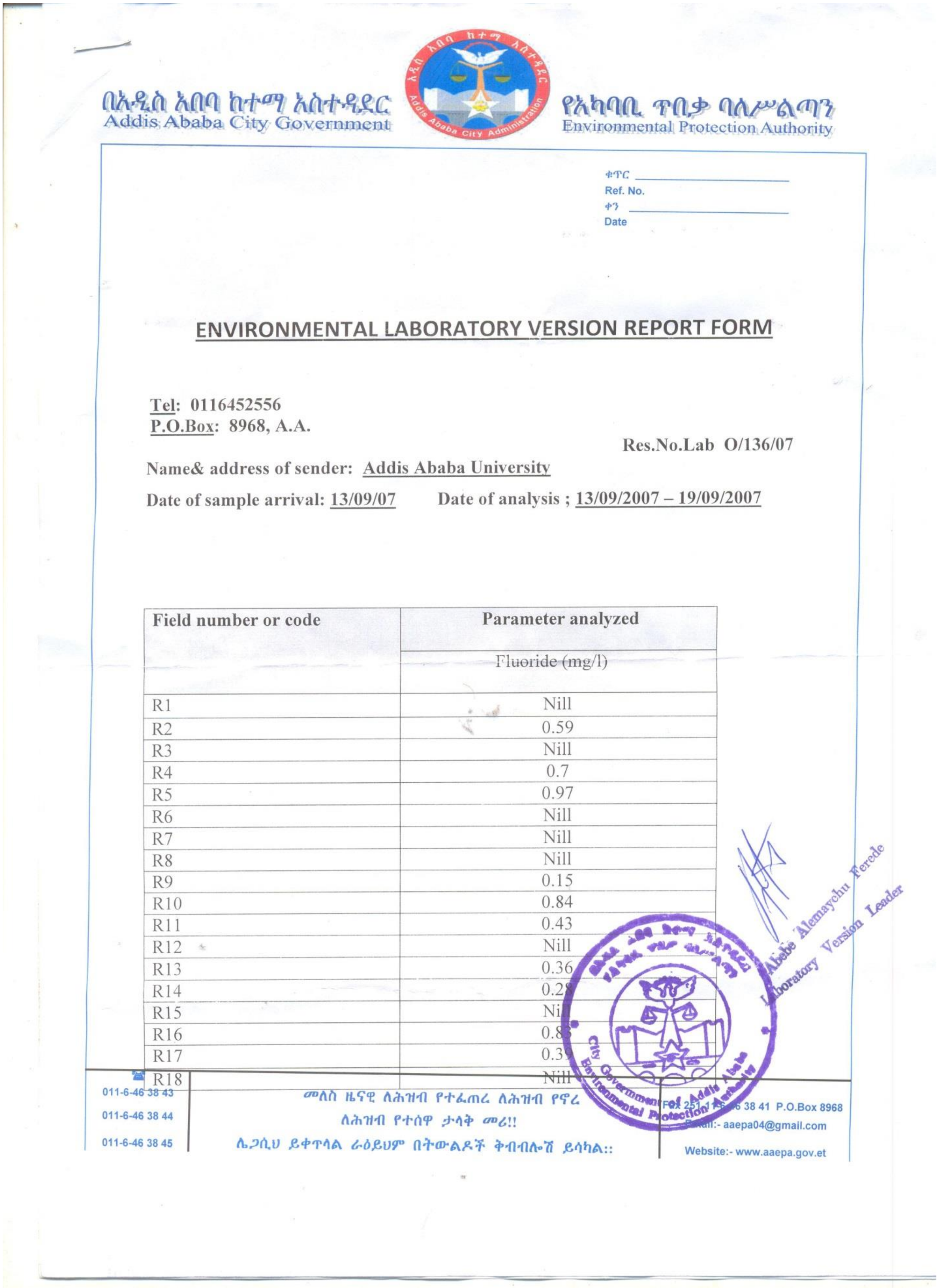
Fax 251-11-6-46 38 41 P.O.Box 8968
Email:- aaepa04@gmail.com
Website:- www.aaepa.gov.et



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Addis Ababa City Government

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Environmental Protection Authority

ቁጥር ____________________
Ref. No.
ቀን ____________________
Date

ENVIRONMENTAL LABORATORY VERSION REPORT FORM

Tel: 0116452556
P.O.Box: 8968, A.A.

Res.No.Lab O/136/07

Name& address of sender: **Addis Ababa University**

Date of sample arrival: **13/09/07** **Date of analysis ;** **13/09/2007 – 19/09/2007**

Field number or code	Parameter analyzed
	Fluoride (mg/l)
R1	Nill
R2	0.59
R3	Nill
R4	0.7
R5	0.97
R6	Nill
R7	Nill
R8	Nill
R9	0.15
R10	0.84
R11	0.43
R12	Nill
R13	0.36
R14	0.28
R15	Nill
R16	0.83
R17	0.39
R18	Nill

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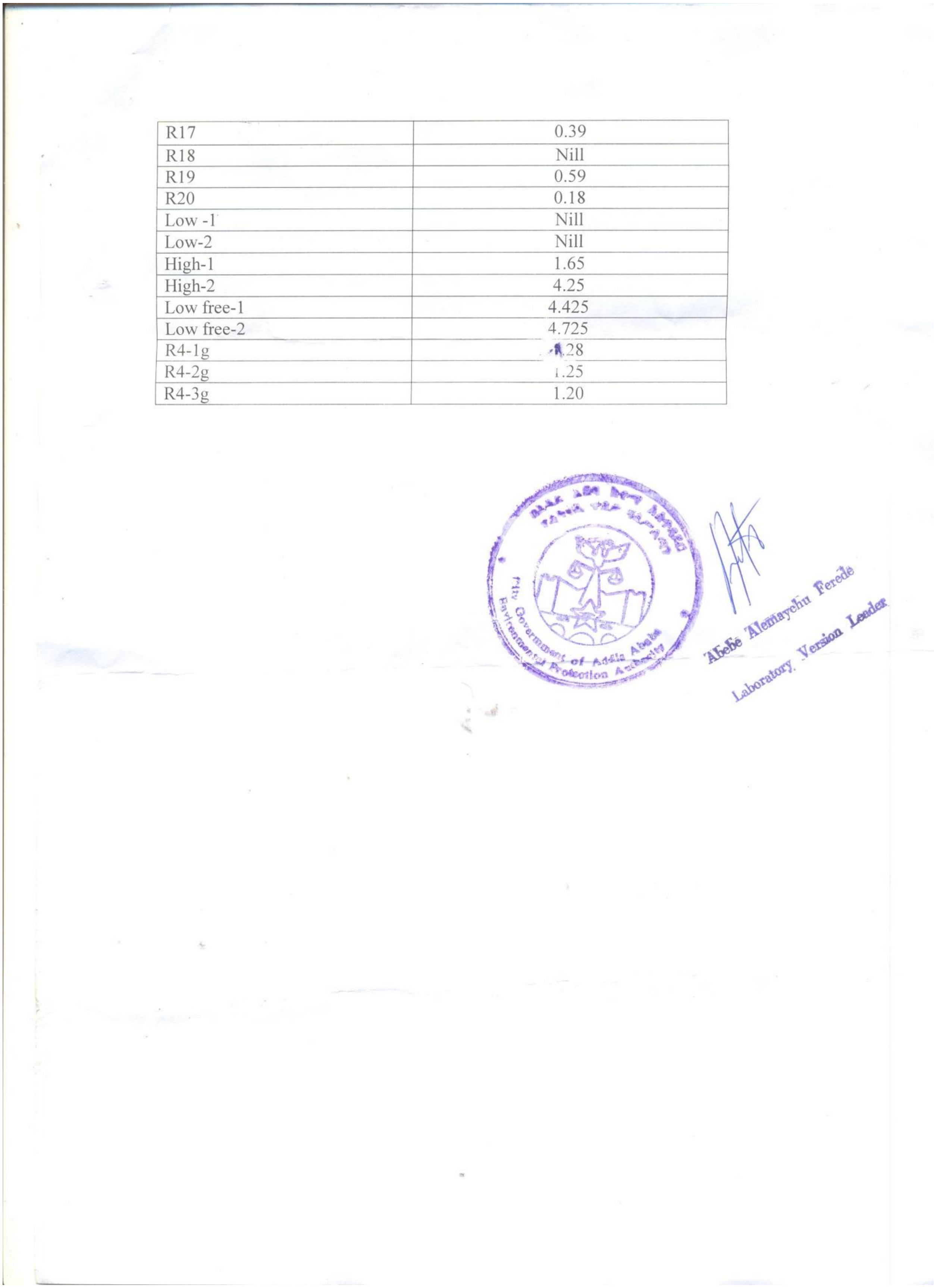
Fax 251 116 46 38 41 P.O.Box 8968
E-mail:- aaepa04@gmail.com
Website:- www.aaepa.gov.et



R17	0.39
R18	Nill
R19	0.59
R20	0.18
Low -1	Nill
Low-2	Nill
High-1	1.65
High-2	4.25
Low free-1	4.425
Low free-2	4.725
R4-1g	1.28
R4-2g	1.25
R4-3g	1.20

City Government of Addis Ababa Environmental Protection Authority

Abebe Alemayehu Ferede
Laboratory Version Leader

DECLARATION

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

July, 2015

Signature (Mitiku Tadele Asra) **Date**