UNIVERSITY OF NAIROBI

DEPARTMENT OF CIVIL AND CONSTRUCTION ENGINEERING

EVALUATION OF FLUORIDE REMOVAL FROM WATER USING BAKED ANDO SOILS

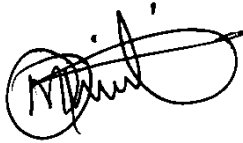**BY**

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A Thesis submitted in Partial Fulfillment of the requirement for Award of the Degree of Masters of Science in Civil Engineering (Environmental Health Engineering) of the University of Nairobi

2023

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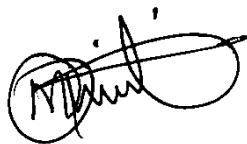Professor Ezekiel Nyangeri

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This work is dedicated to my wife and children.

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ABBREVIATIONS AND ACRONYMS

AEC	Anion-Exchange Capacity
CEC	Cation-Exchange Capacity
EC	Electrical Conductivity
ICP-OES	Inductively Coupled Plasma Optical Emission spectroscopy
NaF	Sodium Fluoride
rpm	rotation per minute
WHO	World Health Organization
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

ABSTRACT

Ingestion of excess amount of fluoride leads to dental and skeletal fluorosis. Because there is no cure for fluorosis, prevention measures such as the reduction of elevated fluoride concentrations from potable water is critical. While several methods for defluoridation exist, accessibility and sustainability challenges such as prohibitive costs and inappropriate technology are major hindrances for removal of fluoride from water among low-income communities. On the other hand, locally available materials such as Ando soil may have potential for removal of fluoride from water. Moreover, soil calcination could enhance the adsorption properties of the soil material in removal of fluoride from solution. This study evaluated baked Ando soil as an adsorbent material for fluoride through batch adsorption tests with the untreated soil as control. Fluoridated water samples were collected from boreholes in Naivasha Town with fluoride concentrations of 7.1 to 7.9 mg/l that exceeded the WHO guideline concentration of 1.5 mg/l for drinking water. Simulated fluoride water samples with fluoride concentrations of 4.4 to 18.4 mg/l were prepared from stock solution. Ando soils samples were collected from Kavutiri in Embu County and subjected to heat treatment at 100 to 700°C for three hours. The highest reduction in fluoride concentration was achieved from 7.1 to 0.5 mg/l in 30 minutes at a dosage 40 g soil L^{-1} borehole water and calcination temperature 350°C. Even though calcination marginally improved fluoride removal rate; nevertheless, it resulted in a more stable adsorption of fluoride ions than the untreated soils. The adsorption data fitted Langmuir adsorption isotherm with the correlation coefficient (R^2) of 0.9769 indicating the calcined soil was a homogeneous adsorbent. The study concluded that baked Ando soil provides a viable alternative for removing fluoride from groundwater sources in Kenya.

1. INTRODUCTION

1.1 Background of the Study

Groundwater is the primary water source for regions with low water potential. The water has generally been considered protected and therefore safe for human consumption. Where treatment has been carried out, it has mostly addressed microbial contamination while less consideration has been given to undesirable chemical properties such as fluoride concentration. Ingestion of excess amount of fluoride contributes to dental and skeletal fluorosis that affects the colour of teeth and the strength of bones. In Kenya elevated fluoride in groundwater is found in a belt stretching from the North through Central and Eastern Regions to the Southern parts of the Rift Valley. Water quality tests conducted on 1,286 boreholes in Kenya indicated 61.4% of the water sources exceeded fluoride concentration of 1 mg/l (Nair et al., 1984). Manji and Kapila (1986) found that wells and boreholes with elevated fluoride levels correlated with high cases of dental fluorosis.

The World Health Organization (WHO) limits the allowed fluoride concentration levels in portable water to 1.5 mgF/l (WHO, 1984). At concentrations greater than 6 mg/l, fluoride consumption increases the risk of skeletal form of fluorosis in both human and animals. However, intensity of fluorosis can be reduced by access to partially defluoridated water (Heifetz et al, 1988).

The available technologies for defluoridation include chemical precipitation, contact precipitation and adsorption/ion exchange. These technologies require expensive chemical materials and technical skills that are only accessible to water supply systems with centralized treatments (Rao et al., 1988; Heidweiller, 1991). For rural communities relying on groundwater sources, the development of cost effective and technically simple processes that use widely available materials is necessary. For example, clay and Ando soils in natural state have shown potential for adsorption of 5.51 mgF/g of adsorbent (Zevenbergen et al., 1996). Additionally, soil subjected to high temperature has shown improved adsorption sites attributed to elimination of water molecules, organic coatings and surface impurities (Gomoro et al. 2012).

This study evaluated the viability of using baked Ando soils as a simple, efficient and affordable method for defluoridation of water.

1.2 Statement of the Problem

Fluoride ions are among the minerals that exist in the natural waters and that are essential for prevention of tooth decay (WHO, 2008). However, over exposure to concentrations above 1 mg/l has a negative impact on human dental and bone health. In many regions of low water potential in Kenya where only groundwater is accessible, fluoride concentrations are higher than allowable limit of 1.5 mg F/l (Nair et al., 1984). Fluoride removal is mainly achieved through contact precipitation, chemical additive, or adsorption/ion exchange. However, accessibility and sustainability of most of the established deflouridation techniques limit application in low-income communities. Therefore, there is need for studies on defluoridation techniques that utilize locally and cheaply available materials such as Ando soils. These soils are available at the local community level and exhibit potential for defluoridation in natural state. Furthermore, there is need to study the potential to improve the adsorption capacity by modification of the Ando soil with heat treatment.

1.3 Objective of the Research

The overall objective of this study was to evaluate applicability of heat modified Ando soils in removal of excess fluoride from water. The specific objectives of the study were to:

1. Evaluate the effect of high temperature modification of Ando soil on adsorption efficiency
2. Establish adsorption isotherms of baked Ando soils in fluoride removal
3. Optimize the calcination temperature, pH and dosing rate for fluoride removal.

1.4 Scope

This study evaluated efficiency of baked Ando soil in removing fluoride from groundwater obtained from Naivasha Town boreholes and laboratory simulated fluoride water. Ando soils for use as the sorbate material was obtained from Muirungi in Nyeri County, Kavutiri in Embu County, Kiarutara C67 Road and Kimakia Forest in Muranga County. The Ando soil materials were characterized before and after baking at 350°C using X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) tests. Adsorption tests assessed the impact of pH, contact time, heat treatment and the adsorbent dosage on the fluoride removal efficiency by the Ando soil before and after baking.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Description of Fluoride

The following sub-sections describe fluoride characteristics, sources and effects on human health.

2.1.1 Properties of Fluorine

The element fluorine has an atomic weight of 18.998 and occurs as diatomic gas in its elemental form with valence number 1. Fluorine is absent in its elemental state due to its high reactivity. It forms fluoride ions F^- in aqueous solution with an oxidation state of negative one. Its ionic radius is similar to that of hydroxyl ion.

2.1.2 Sources of Fluoride in water

Fluoride is released into the atmosphere through volcanic eruptions and industrial emissions. It is present in the atmosphere as aerosols, which combine with precipitation and is subsequently deposited on the surface of the earth. Fluoride containing fertilizers and pesticides when applied to soil increase concentration of fluoride in soil, which gradually leaches down and contaminates groundwater.

Fluoride is found in natural water but concentrations depend on the location and the type of the water source. Geological sources are the main contributors to occurrence of fluoride in water though man-made sources are significant. Seawater fluoride concentrations are about 1 mgF/l while lower than 0.5mg/l of fluoride levels are found in rivers and lakes (Fawell, 2002). Because leaching influences fluoride movement in geological materials, groundwater fluoride levels can be either low in areas without fluoride rich materials or high in aquifers with rocks containing fluoride minerals. Groundwater in soils or rocks with low calcium is likely to have higher fluoride concentrations (Edmunds and Smedley, 1996). There are four main possible sources of fluoride in groundwater; namely, aquifer materials, volcanic ash, fly ash and fertilizers. The following sub-sections detail the different pathways of fluoride to the groundwater.

2.1.2.1 Aquifer Materials

Weathering of fluoride containing rocks contributes to the fluoride presence in groundwater. Notable fluoride containing minerals in rocks and sediments are fluorite, fluorapatite, biotite mica, amphiboles, cryolite, villiaumite and topaz (Chae et al., 2007). Fluoride is released to the aquifer during weathering process and its concentrations depend on the period of interaction. Abundant biotite and amphiboles release the highest amount of fluoride in the water bodies. In Kenya, fluoride in natural waters is mainly caused by weathering and breakdown of fluoride rich volcanic rocks (Gaciri and Davies, 1993).

2.1.2.2 Volcanic and Fly Ash

Hydrogen fluoride is released naturally from volcanic activities (D' Alessandro, 2006) Fluoride released in the atmosphere returns to the soil by mixing with air moisture and rainfall. This fluoride percolates though the soil to the groundwater contributing to increased concentrations.

2.1.2.3 Farm inputs

The phosphate rock used in the manufacturing of fertilizers has high fluoride content. When fertilizers are added to the soil, the chemical material eventually percolates to the groundwater increasing fluoride concentrations (Farooqi et al., 2007). Additionally, pesticide containing fluoride element increases its concentration in the soil and groundwater (Poovaiah, 1988; Ware, 1975).

2.1.3 Beneficial application of fluoride in human

The main benefit of fluoride in water to humans is reduction of cavities. Fluoridated water provides protection to the tooth through formation of fluoroapatite on the enamel that deters the decay process. For good health, recommended concentrations of fluoride ranges from 0.5 to 1.0 mg/l (WHO, 2008). Accordingly, fluoride is added to toothpaste and drinking water in some centralised water supply treatment for dental health.

2.1.4 Risks of fluoride in human

Ingestion of water containing fluoride above the recommended fluoride concentrations leads to dental and skeletal fluorosis. The condition can be acute or chronic depending on the amount consumed and how long the ingestion has taken place. Globally, there are a total of 200 million people with fluorosis (Ayoob and Gupta, 2006).

2.2 Methods for defluoridation

Because fluoride ingestion risks permanent fluorosis, which has no known cure, its removal from water to prevent ingestion is the only viable option (Sahli et al., 2007). Available defluoridation methods can be classified as:

    a. Chemical additives

    b. Contact precipitation

    c. Adsorption/ion exchange

The following sub-sections describe the three defluoridation methods in details.

2.2.1 Chemical additive methods

Soluble chemicals are added to the water to remove fluoride through precipitation. The precipitate occurs as fluoride salt while in some instances, especially in the presence of aluminium ions such as from alum, flocculation is observed. The additive chemicals include alum $(KA1(SO_4)_2 12H_2O)$, alum and lime (CaO), lime softening $(Ca(OH)_2)$ and calcium chloride $(CaCl_2)$. Nalgonda defluoridation technique method utilizes an aluminium sulfate-based coagulation-precipitation-sedimentation-filtration process. Alum $(Al_2(SO_4)_3 18H_2O)$ is mixed with fluoridated water as a coagulant to form an insoluble aluminium hydroxide $(Al(OH)_3$. Larger quantities of alum are required to remove fluoride (150 mg/mgF$^-$) compared with the normal amount used for water treatment (Leela Lyengar, 2003). The process of removing fluoride is achieved when negatively charged fluoride ions are adsorbed onto insoluble aluminium hydroxide materials which are then removed by settling and filtration (Dysart 2008; Fawell et al., 2006). Lime is used for maintaining neutral pH.

2.2.2 Contact precipitation methods

In contact precipitation method, calcium and phosphate materials are used to remove fluoride from a solution through precipitation thus forming calcium fluoride and/ or calcium fluorophosphate. However, this process is slow, which makes the precipitation process difficult unless with a catalyst. Saturated charcoal medium, for example, bone charcoal is used to catalyze the precipitation of fluoride. The bone charcoal also functions as a filter media for the precipitate (Fawell et al., 2006; Dahi, 1997).

2.2.3 Adsorption/ion exchange methods

Adsorption is a mechanism where attachment occurs at the surface of the adsorbent (Pouran et al., 2020; Milan, 2014). Fluoridated water is passed through a material with a fluoride binding agent and fluoride ions captured by physical, chemical or ion exchange mechanisms (Suneetha et al., 2015). During the adsorption process, the adsorbent agent is saturated over time and requires regeneration to activate the adsorption sites. The adsorption process takes place when there is exchange of hydroxyl or other anionic groups with fluoride (1 g Lyengar, 2003). In this method, fluoride removal efficiency is affected by the initial concentration of fluoride, pH, contact time, type of absorbent and its size.

Ion exchange takes place between two electrolytes or in an electrolyte and a complex material. Some of the ions exchanging agents are ion-exchange resins, zeolites, clay and soil.

The following are materials commonly used in the adsorption process:
1. Activated Alumina (Al_2O) $_3$
2. Fluidized Activated Alumina
3. Activated Bauxite (Hydrate of Al (OH) $_3$)
4. Zeolite ($NAO_2.Al_2O_3$), n SiO_3xH_2O
5. Tricalcium Phosphate ($Ca_3 (PO_4) _2$ or TCP)
6. Super Phosphate ($COHPO_4 + CaSO_4$)
7. Activated bone Char ($Ca_{10}(PO_4) _8OH_2$)
8. Magnesite ($MgOO_3$)
9. Activated Carbon
10. Palan Carbon
11. Charcoal
12. Clay and Soil
13. Bricks

Among other methods of defluoridation, adsorption techniques are highly adaptable with regard to cost effectiveness, minimum environmental impact, acceptability and usage.

2.2.4 Theory of adsorption

The adsorption process involves formation of a thin layer of the adsorbate from its vapour or solution onto an adsorbent (Chiou, 2002). The formed film of the adsorbate has several layers

for the gas phase adsorption while the liquid phase adsorption is usually a single layer. The adsorption process is enhanced by availability of adsorption sites in a larger surface area. If the adsorption occurs and the chemical characteristics of the solid and adsorbate are maintained, it is called physical adsorption. If there is chemical reaction in the adsorption process and is characterized by transfer of electrons or further breakdown of the chemical bonding forces, the adsorption is referred to as chemisorption (Chiou, 2002).

Adsorption isotherms are applied for the quantitative evaluation of the adsorbent capacity where the amount of the adsorbate is considered at a constant temperature and equilibrium concentration of the substrate. When analyzing vapour adsorption, the adsorbed mass on the solid surface corresponds to the solid mass. The vapour adsorption depends on the temperature, pressure, and the characteristics of the solid and vapour. Due to diverse nature of the solid surface, the adsorption energies also tend to vary (Chiou, 2002). As a result, the surface area will influence the amount of vapour adsorbed; increasing the surface area will lead to enhanced adsorption.

2.2.5 Description of adsorption Isotherms

A wide variety of equilibrium isotherm models can be categorized based on kinetic approach, thermodynamic and potential theory (Malek and Farook, 1996). Kinetic approach is the adsorption and desorption rates that are equal at equilibrium whereas thermodynamics provide a platform of deriving adsorption isotherm models considering the temperature, pressure and volume parameters. The potential theory defines the process of generating the characteristic curve.

Langmuir, Freundlich, and Temkin are the common models applied in adsorption. The following section elaborates details of these isotherm models, and their application and characteristic equations.

2.2.5.1 Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm can be considered to fall under chemisorption process. It assumes that adsorption occurs at specific homogenous sites within the adsorbent by monolayer sorption, without interaction between adsorbate molecules. Once the adsorption is achieved at a particular site, there is no subsequent adsorption. It further assumes that all sites have similar

energy and rules out activity between the adsorbate species. Based on the assumption above, Langmuir Isotherm is described as:

$$Q = \frac{Q_m bP}{1+bP}$$
(2.1)

where:

Q_m is the limiting adsorption capacity,

$b=k_a/k_d$

k_a is the adsorption rate constant

k_d is the desorption rate constant

P is the partial pressure

According to Kumar 2006, there are four linearized equations of the Langmuir Isotherm as shown in Table 2.1.

Table 2.1. Langmuir equilibrium isotherms (Lima et al., 2015)

Non Linear form	Linear form	Plot
$qe = \dfrac{Q_{max} K_L C_e}{1 + K_L C_e}$ Langmuir	$\dfrac{C_e}{qe} = \dfrac{1}{K_L Q_{max}} + \dfrac{1}{Q_{max}} C_e$ Langmuir-1	$\dfrac{C_e}{qe}$ versus C_e
	$\dfrac{1}{qe} = \dfrac{1}{Q_{max}} + \left(\dfrac{1}{K_L Q_{max}}\right)\dfrac{1}{C_e}$ Langmuir-2	$\dfrac{1}{qe}$ versus $\dfrac{1}{C_e}$
	$qe = Q_{max} - \left(\dfrac{1}{K_L}\right)\dfrac{qe}{C_e}$ Langmuir-3	qe versus $\dfrac{qe}{C_e}$
	$\dfrac{qe}{C_e} = K_L Q_{max} - K_L qe$ Langmuir-4	$\dfrac{qe}{C_e}$ versus qe

2.2.5.2 Freundlich Equation

The Freundlich equation assumes correlation between the adsorbate concentrations on the adsorbent surface with increased adsorbate concentration. Unlike the Langmuir isotherm, the

model recognizes adsorption to occur through multiple layers. Equation 2.2 shows the Freundlich isotherm model;

$$qe = K_F C_e^{1/nF}$$ (2.3)

where

K_F is the Freundlich equilibrium constant (mg g^{-1}(mg L^{-1})$^{-1/n}$),

n_F is the Freundlich exponent (dimensionless).

The linear form of the Freundlich isotherm is as follows:

$$\log qe = \log KF + \frac{1}{n}\log Ce$$ (2.4)

where

$1/n$ is adsorption intensity

2.2.5.3 Temkin Isotherm

The Temkin Isotherm model recognizes indirect adsorbate/adsorbate interactions and how they impact on the adsorption process. The model points out that the heat of adsorption decreases linearly with increased surface coverage within the layer. The Temkin isotherm is valid only for an intermediate range of ion concentrations. The Temkin isotherm model equation is written as:

$$q_e = \frac{RT}{b}lnK_T + \frac{RT}{b}lnC_e$$ (2.4)

where

b is Temkin constant

K_T is Temkin isotherm equilibrium binding constant (Lg^{-1})

q_e is adsorbent capacity (mol g^{-1})

C_e is the equilibrium concentration (mol L^{-1})

R is the universal gas constant (8.314 J K^{-1} mol-^{1})

T is the absolute temperature (K)

2.3 Occurrence and Description of Ando soils

Five major types of soils are found in Kenya namely; loamy, sandy, alluvial, black cotton and volcanic soils. Volcanic soils are also referred to as the red earth soils. Ando soils is a volcanic type of soils that is generally found along mountains, scarps, hills, volcanic foot ridges and in areas with pyroclastic rocks from recent volcanoes as illustrated in Figure 2.1.
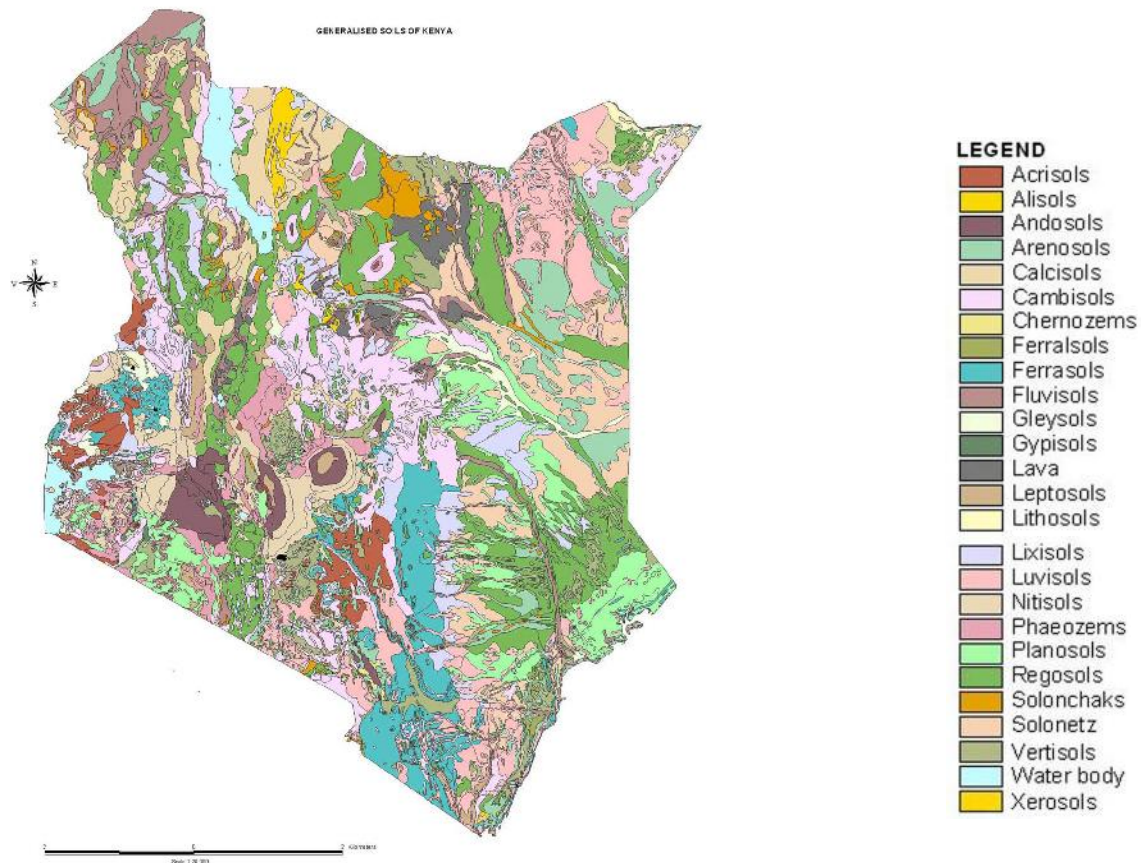
Figure 2.1. Generalised soils of Kenya (Ministry of Agriculture Soil Survey, 1980)

2.3.1 Description of Ando Soils

Ando soils are developed in the pyroclastic material, notably volcanic ash (Neall, 1985). The prefix Ando indicates a low bulk density and the presence of volcanic ash. The most distinctive property is the presence of active forms of aluminium in an aluminium humus complex of allophane and imogolite (Wada, 1985). Ando soil contains varied concentrations of aluminium, iron and silica elements that allow adsorption of fluoride ions (Maurice and Hitoki, 2006). The soils adsorb fluoride with the release of the hydroxyl ions (Mizota and Reeuwijk, 1989). Ando

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soils are formed through the weathering process in the presence of organic materials. Variable charge characteristics primarily result from noncrystalline materials and soil organic matter. The soil cations are attached through electrostatic forces by the negative charge of the soil material. The attached cations are easily exchangeable in soil solution where the exchange sites are mainly on clay minerals and organic matter. During the weathering process, liberated cations are washed out but aluminium and iron ions are attached to stable complexes with humus (Mizota and Reeuwijk, 1989). In mild to low pH conditions, aluminium precipitates with silica to form allophane and imogolite while iron forms ferrihydrite (Wada 1977).

2.3.2 Properties of Ando soils

The following sub-sections describe the characteristics of Ando soil in natural state.

2.3.2.1 Morphology

Ando soils have dark colours with varied visual appearance between the top soil and the subsoil. The soil fit into AC or ABC profile (Figure 2.2) where A-horizon is between 20 to 50cm in thickness. Sometimes the thickness can go beyond 50cm up to 100cm or below 20cm. The dark colours are more prevalent in cooler climatic zones compared to the tropical regions where organic matter accumulation is lower. The organic matter averages 8% with the highest reaching 30% depending on the soil profile (Mizota and Reeuwijk 1989). The soils have interstices, which offer conducive properties for adsorption process.
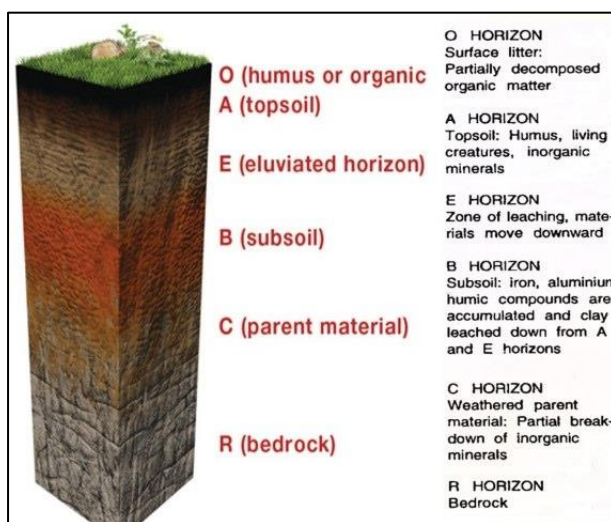
Figure 2.2. Soil horizons (Indian Geography by Kullar)

2.3.2.2 Mineralogy

Ando soils mineral content varies because of the soil horizon, properties of the volcanic parent material, pH, water content, size of ash deposits and buildup of organic matter (Mizota and Reeuwijk 1989). The clay material in the Ando soils often comprise of allophane and rarely the imogolite. In other cases, it will be made of humus complexes of aluminium and iron together with opaline silica. Besides primary minerals, other components in clay can be ferrihydrite, halloysite and kaolinite, gibbsite, silicates and intergrades.

2.3.2.3 Physico-chemical properties

Ando soil cation-exchange capacity (CEC) increases with pH while the anion-exchange capacity (AEC) decreases. Exchangeable acidity in the soil indicates the quantity of hydrogen (H^+) and aluminum (Al^{3+}) cations and both exchange sites of attachment in the soil media. At higher pH above 5, clay materials comprise mainly of the allophane and imogolite while at pH below 5, humus, aluminium and iron complexes are present. Exchangeable aluminium is available at lower pH (Mizota and Reeuwijk 1989). The reactive sites of Ando soils are likely to have amorphous compounds of aluminium, silica and humus. The chemical reactivity of the Ando soil can be attributed to the active aluminium sites within the soil material and may be present in several forms such as paracrystalline aluminosilicates (allophane and imogolite), interlayer hydroxyl-alluminium ions, aluminium-humus complexes or exchangeable aluminium ions. Reaction with fluoride leads to liberation of hydroxyl ions. The soils have a low bulk density of less than 0.9 g/cm^3 while the water content at a pressure of 1500 KN/m^2 is greater than 20% (Mizota and Reeuwijk, 1989).

2.3.3 Past studies on use of Ando soil as an adsorbent

Analysis of Ando soils from Kenya using Langmuir isotherm model indicated fluoride adsorption capacity of 5.51 mg/g (Zevenbergen et al., 1996). The technical application test demonstrated that Ando soils could be economically and efficiently applied in de-fluoridation of potable water on a limited scale. Other studies on fluoride removal by Ando soils were not available.

2.4 Soil adsorption properties

Soil comprises clay, silt, sand and organic matter (Masami and Hitoshi, 2018). Clay and organic matter have negatively charged sites and therefore hold cations (Neary et al, 2008).

Within the organic matter, where cations are held together in the soil, the soil comprises colloids, which influence its physical and chemical properties (Neary et al, 2008). The colloids are mobile due to charges on their surface and can absorb gases, liquid and solid from their suspension. They have properties of cohesion and adhesion (Enos and Audre, 2019). Some of the colloids such as refined clay particles are minerals, whereas others are organic (Enos and Audre, 2019). The colloids are suspended in water which causes murkiness. Soils with high clay particles have higher ability for adsorption of fluoride due to presence of kaolinite, vermiculite, and montmorillonite that have very strong sorption capacity (Ifeoma and Onyedikachi, 2021). The chemical content of certain hydrous silicates and cations such as aluminium and iron also influence the adsorption of fluoride (Neeraj and Chandra, 2021).

2.5 Effect of soil calcination

Although naturally occurring Ando soils exhibit significant capacity for removal fluoride from water, investigation by Hauge et al. (1994) on fired clay at temperatures between 500 and 1000 °C found clay products with favorable fluoride removal properties at 600 °C calcination. An increase of calcination temperature above 600 °C reduced adsorption while at 900 °C and above the burnt clay was unable to remove fluoride. At 200 °C, the soil organic matter started to disintegrate and was completely eliminated at 400 °C. The organic matter is essential in retention of water in the natural soils while clay is important in buffering the soil pH. At higher temperatures, the soil clay content is reduced resulting in a tendency to exhibit sandy properties, which is not favorable for adsorption of fluoride. Moreover, the soil pH characteristics are altered.

2.6 Implications of literature review

The literature review showed adsorption to be the most widely applied method of defluoridation because of its ease of operation and cost effectiveness. Ando soil as an adsorbent has been demonstrated to remove fluoride from water. The liberation of hydroxide from the soils correlates with amount of alumina in the soil while non-crystalline materials in the soil adsorb higher amount of fluoride (Perrot et al, 2006). Calcination has been proved to increase the adsorption capacity of soil material. Because defluoridation studies with calcined Ando soil are not available, there is need to evaluate the fluoride adsorption properties of the soils calcined at different temperatures.

CHAPTER THREE

3. RESEARCH METHODOLOGY

3.1 Overview of Methodology

This Chapter describes the steps and processes for removing fluoride from groundwater and simulated fluoridated water by thermally treated Ando soils. Fluoride water was obtained from boreholes and shallow well in Naivasha Town while simulated fluoridated water was made from diluted stock solution of sodium fluoride. Ando soil samples were collected from Mt Kenya and the Aberdare Ranges sites that are known to have the type soil. The adsorbent soil samples were characterized in pristine state and after thermal treatment. Adsorption tests were conducted to measure the efficiency of fluoride removal by Ando soil at different contact times, pH, sample quantities and calcination temperature.

3.2 Fluoride Water Sampling

Water point samples were taken from two private boreholes and a shallow well in Naivasha Town. The borehole water is used by local community while the shallow well water is used for washing vehicles. Based on the existing data on Naivasha area groundwater, the water points have high fluoride concentrations in the range 0.09 - 43.6 mg/l (Olaka et al, 2016). The water samples were analysed for flouride and the samples with the highest fluoride concentration levels selected for adsorption test.

Simulated fluoridated water samples were prepared using the laboratory reagents to achieve fluoride concentration greater than the groundwater samples to assess fluoride adsorption by Ando soil for concentration above 7.9 mg/l. Fluoride stock solution of 100 mg/l was prepared by dissolving 0.221 g of sodium fluoride in 100 ml of distilled water. Subsequent working solutions were obtained from this stock solution. The highest fluoride concentration prepared was 18.4 mg/l just below the maximum concentration reading of the high range fluoride photometer.

3.3 Ando Soils Sampling

In Kenya, Andosols are found along the slopes of the Chyulu Range, the Rift Valley, Mount Kenya and Aberdare Ranges (Muchena and Gachene, 1988). Soil samples were obtained at locations along Mt Kenya and the Aberdare Ranges where annual rainfall is above 1000 mm. The samples were collected along the road reserve where soil has not been disturbed over time.

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The soils sampled areas have been subjected to leaching due to soil erosion as a result of the steep terrain and rainfall thereby exposing the underlying soil that exhibit andosol properties.

Four set of soil samples were collected for adsorption tests from Muirungi in Nyeri County, Kavutiri in Embu County, Kimakia forest and Kiarutara C67 road in Murang'a County (Figure 3.1). The soil samples were collected at a depth ranging between 30 and 60 cm to exclude top soil matter. A crowbar was used to soften the top surface soil and a metal trowel was used to scoop out the soil. The soil samples were collected in clean dry bucket containers and transferred to the laboratory for analysis and processing for adsorption tests. Soil samples for determining bulk density were collected using a metallic tube of 75 mm internal diameter and 80 mm length.
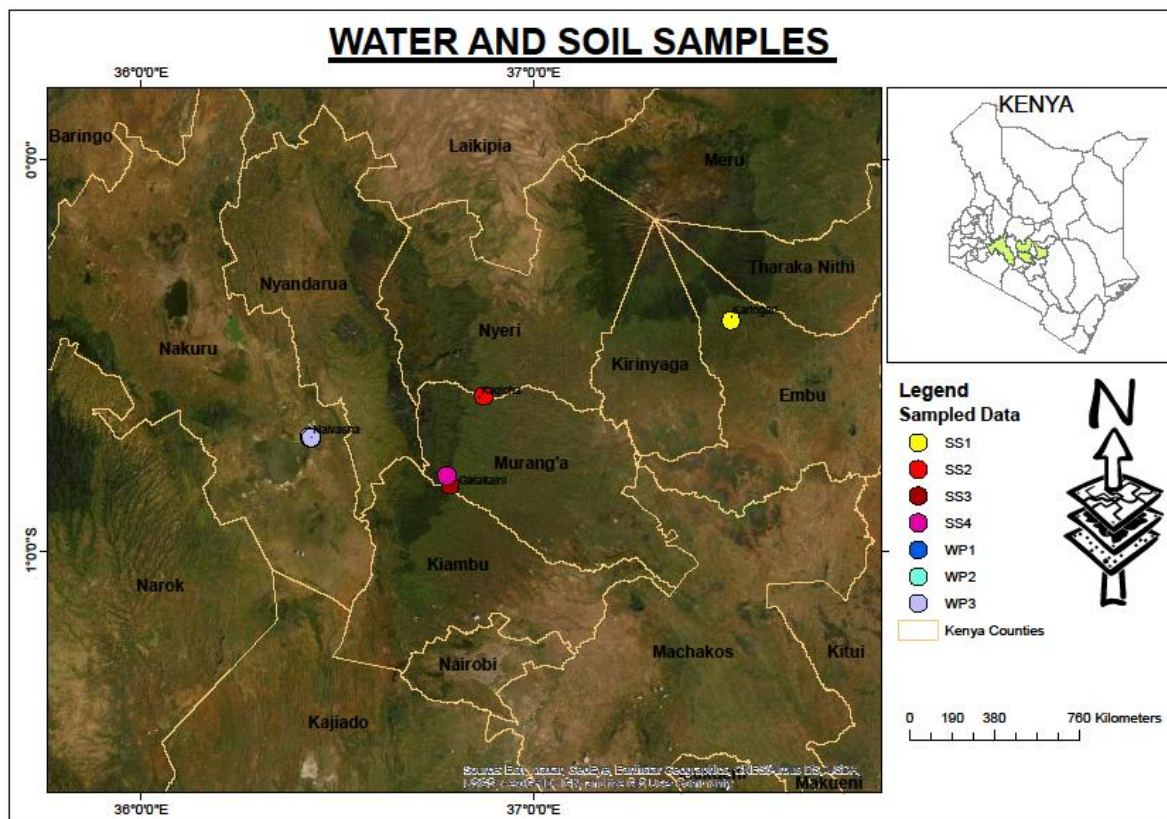
Figure 3.1. Ando soils and fluoride water sampling locations

3.4 Analysis of untreated Soil Samples

Air-dry fine Ando soil was analysed for ion exchange, exchangeable acidity, material constituents, soil pH, bulk density, texture composition and electrical conductivity (EC) as described in the following sub-sections.

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3.4.1 Ion exchange properties: CEC

Mehlich 3 method (Ross and Ketterings, 2011) was used to determine the cation exchange capacity (CEC), which is an indicator of colloidal clay and/or presence of organic matter. The CEC was estimated by calculating the amount of the Ca^{2+}, Mg^{2+} and K^+ ions extracted by using Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES) analytic technique. Because of the low pH of the soil, exchangeable acidity Al^{3+} was included in the cations.

3.4.2 Exchangeable acidity (exchangeable aluminium content)

Titration method was used to determine exchangeable acidity by titrating a potassium chloride extract of the soil (Bruce, 1997). The exchangeable ions on soil exchange sites were transferred into solution for measurement by flooding the active sites of the soil with ions from a strong salt solution extractant. The extractant, and exchanged soil ions, was separated from soil and then analyzed for the exchangeable aluminium ions. Exchangeable aluminium was determined by using standardized base after leaching the soil sample with potassium chloride. A 1:10 soil: extractant volume ratio was used.

3.4.3 Soil texture determination: clay, silt and sand contents

Hydrometer method (ASTM D7928, 2021) was used to establish the clay content in the soil. Measurement applied the relationship between of particle size or radius and the sedimentation rate, based on Stoke's law and is dependent upon liquid temperature, viscosity, the diameter and specific gravity of the falling soil particles. Soil suspension was dispersed with sodium hexametaphosphate before settlement. Hydrometer measurements were then taken and related to the amounts of sand, silt and clay in the soil.

3.4.4 Soil pH

The soil pH was determined through potentiometric method (Kalra, 1995) by determining the potential between two electrodes measured using a high impedance voltmeter on a soil suspension of 1:2 water to soil ratio.

3.4.5 Soil bulk density

The cylindrical core method (volumetric cylinder method) (Gatea et al, 2018) was used to determine bulk density of the soil which is a common method of measuring dry soil bulk density. A cylindrical metallic core measuring 80mm in diameter was driven to 75mm depth inside the soil to collect two soil samples for each of the four sites. The soil samples were stored

in a polythene bag before taking it to the laboratory and tested for the wet mass. The samples were then oven dried at 105°C for 24 hours to remove the moisture before the dry weight was determined. The bulk density ρ_b was calculated by:

$$\rho b = \frac{m}{v} \qquad\qquad (3.1)$$

Where

m is the oven dried soil mass and

v is the core volume ($v = \pi r^2 h$).

r is the radius of the core and h is the soil depth.

3.4.6 Electrical Conductivity

The electrical conductivity, that indicates the intensity of soluble (salt) ions in soil, was measured using potentiometric method (ASTM E1004, 2017). A conductivity cell was used to measure the electrical resistance of a 1:2 soil: water suspension, after air drying the soil sample.

3.4.7 Soil constituent elements

Elemental analysis of Ando soils were carried out using Mehlich 3 method (Zbiral, 2016) at the Crop Nutrition Laboratory (Cropnuts) in Limuru. The elements include potassium, phosphorous, calcium, magnesium and sodium. The elements were extracted from the soil using ammonium nitrate and nitric acid. The extracted major and minor elements were measured at the soil analysis laboratory with inductively coupled plasma optical emission spectroscopy (ICP-OES). The process comprised exciting the atoms leading to movement of electrons from lower to higher energy level which later return to low energy position releasing emission rays (spectrum rays) and the emission rays corresponding to photon wavelength were measured. The element type was indicated by the position of the photon rays and the concentration of each element determined from the intensity of the rays.

3.5 Soil Calcination

Alteration of the physical or chemical composition was carried out through calcination without fusion of the soil material by heating the soil samples. The physical and chemical changes in the heated soil was expected to enhance the adsorption efficiency by influencing the properties

of adsorption sites. Collected soil samples were weighed prior to the heat treatment to assess weight loss when subjected to different temperatures. The samples where then thermally treated at different temperatures using the digital Muffle furnace, model FHX-27. Soil samples were placed in porcelain crucibles, and heated at different temperatures ranging from 100 to 700 ˚C for three hours and allowed to cool overnight. Soil samples were weighed after heat treatment to assess any loss occurring after calcination. The calcined samples were observed for colour and texture changes as a result of calcination before storage in closed containers until application for adsorption tests.

3.5.1 Effects of heating on the Soil

X-ray fluorescence (XRF) and X-ray diffraction (XRD) tests were carried out to assess the changes in the soil when subjected to heat treatment. Both tests were carried out at the Mines and Geology Department laboratory at Ministry of Mining. The XRF method was used to determine the quantative elemental composition of soil samples both in pristine state and baked at 100 to 700°C. In XRF, characteristic secondary X-rays are produced when soil sample is subjected to high-energy from X-rays or gamma rays. Emitted radiation, which indicate energy characteristic of the atoms present, was used to determine the proportion of element composition in a material. The intensity of dispersive energy and wavelength of each characteristic radiation were measured and related to sample elemental composition.

The XRD analysis was used to determine the crystallographic structure of the soil material. The test samples were irradiated with incident X-rays and the intensities and scattering angles of the X-rays leaving the material measured.

3.6 Fluoride Adsorption tests

The fluoride adsorption tests were carried out for the pristine and baked Ando soil samples using batch tests of different weights of soils added to 50ml of fluoride water. Four test parameters; namely, pH, contact time, adsorbent dosage, and stirring were varied to test adsorption efficiency of Ando soils for fluoride. The Ando soil and fluoride water suspension were left to stand for predetermined lengths of time and then filtered using WhatmanTM 12.5cm Grade 1 qualitative cellulose filter paper before determining residual fluoride in water. However, samples with high turbidity were centrifuged before filtration to reduce interference of fluoride photometer readings. Fluoride concentration was determined using the HANNA

fluoride high range photometer, 96739 by mixing the filtered suspension with high range reagent A (93739A-0) and B (93739B-0).

3.6.1 Effect of calcination on adsorption

The influence of calcination on defluoridation was assessed with 2 g of Ando soil sample mixed with 50ml of fluoride water for untreated and baked samples in two stages. The first stage of tests was carried out on samples baked at interval of $100°C$ in the temperature range of 100 to $700°C$. The second stage of test was carried out for samples baked at temperatures of 350 to $450°C$. The optimum calcination temperature for adsorption was identified and used for the subsequent adsorption tests.

3.6.2 Effect of stirring adsorbent-adsorbate suspension on adsorption

Both intermittent and continued agitation of the batch reactor suspensions were carried out to vary solid-liquid surface contact. The suspensions were agitated using magnetic stirrer (MSH-20D) at speeds of 100, 200, 300, 400, 500, 600 and 600 rotations per minutes. Filtration of the stirred samples was carried out using the micro cellulose filter paper. In instances where the turbidity did not clear up, centrifuging was carried out before testing for residual fluoride in suspension.

3.6.3 Effect of pH on adsorption

The pH level was adjusted to analyse its effect on adsorption efficiency on both the untreated and thermally treated soil samples. The pH was lowered using HCl 0.1M and raised using 0.1M NaOH to predetermined values measured by pH meter. The samples were prepared by adding 0.15 and 2 g of Ando soil samples to 50 ml of fluoride water. The fluoride concentration was measured after 30 minutes for the reactor pH.

3.6.4 Contact time adsorption tests

Tests on variation adsorption with contact time were conducted on 2 g of soil sample with 50ml of fluoride water. Adsorption was tested for contact time duration of 30, 60, 120, 180 and 240 minutes. Stirring was carried out intermittently at intervals of 10 minutes and continuously for different reactors.

3.6.5 Ando soils dosage adsorption tests

The effect of varying Ando soil dosage on fluoride adsorption was assessed by mixing different 0.5, 1, 2, 4 and 6 g of untreated and heat-treated soil at 350°C with 50ml of fluoride water. The suspension was agitated intermittently at 10 minute intervals and the residue fluoride concentration measured after 30 and 60 minutes.

3.7 Modelling of Adsorption Isotherms

The equilibrium concentration C_e (mg/l) at equilibrium time of fluoride in the filtrates was determined for each selected initial concentration, C_i (mg/l). The adsorbent loading at equilibrium, q_e was calculated as the amount of the fluoride removed per unit mass of the adsorbent in mg/g. To obtain multiple results for equilibrium concentration from a wide range of fluoride concentrations, results of adsorption tests on simulated fluoridated water at 0.15g in 50ml simulated fluoridated water at pH of 2.06 in 3 hours contact time were included.

The test data was then fitted to the linearized Langmuir, Freundlich and Temkin isotherm models. Linear regression coefficients (R^2) from the graph was used to establish the isotherm model which best fitted the study data.

4. RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter presents the results and discussions of characterization of Ando soils and adsorption tests for fluoride removal from water using Ando soils in pristine and calcined state. The adsorption tests cover temperature of calcination, soil dosage, contact time, pH and agitation of the suspension. The fluoride adsorption is then fitted to the Langmuir, Freundlich and Temkin adsorption isotherms.

4.2 Properties of fluoride water samples

Water samples collected from two boreholes and a shallow well from Naivasha Town had fluoride concentration ranging from 5.5 to 7.9 mg/l (Table 4.1), which exceeded the WHO guideline values of 1-1.5 mg/L. Borehole BH1 was selected for sampling for deflouridation tests because of its higher fluoride concentrations.

Table 4.1. Fluoride water samples sources and concentration level

Source	Location	Samples collected	Fluoride concentration (mg/l)
Borehole BH1	Seasons Supermarket	BH1_S1	7.1-7.9 Average =7.34
Borehole BH2	Rumax building	BH2_S1	5.7
Shallow well (SW)	Seasons Supermarket	SW_S1	5.5

Apart from the high fluoride concentrations, other quality parameters for the borehole water were within the allowable WHO standards for drinking water (Table 4.2). The analysed samples indicated moderate presence of hardness as calcium carbonate at 72 mg/l, alkalinity as calcium carbonate 370 mg/l, sulfates 150 mg/l and chlorides 156 mg/l. The dissolved solids concentration of 760 mg/l was high but within acceptable standards of drinking water. The

presence of different minerals in the borehole could be attributed to reaction of water with minerals in the underground rocks and sediments. The borehole water mid-range conductivity (892 µS/cm) indicated presence of conductive ions from dissolved salts and inorganic materials such as alkalis, sulfides, chlorides and carbonates compounds.

The simulated fluoridated water sample had total alkalinity as calcium carbonate 35 mg/l, chlorides 10 mg/l and dissolved solids 230 mg/l. The limited presence of minerals in the simulated fluoridated water was because of the absence of minerals from the de-ionised water except for the sodium fluoride used to make the stock solution. Additionally, the simulated fluoridated water conductivity of 387 µS/cm was lower than that of the borehole water of 892 µS/cm which was attributed to fewer ions in the deionized water.

Table 4.2. Chemical and physical analysis of borehole BH1 water

Parameter	Borehole water sample	Stock solution sample	Allowable amount in drinking water by WHO
pH	6.7	6.89	6.5-8.5
Fluoride mg/l	7.2	7.2	1.5
Conductivity µS/cm	892	387	2500
Turbidity, FTU	0.21	0.01	5
Total hardness as $CaCo_3$, mg/l	72	0	500
Total Alkalinity as $CaCo_3$, mg/l	370	35	500
Iron, mg/l	0.1	0	0.3
Sulphates, mg/l	150	0	400
Nitrates, mg/l	4	0.2	10
Chlorides, mg/l	156	10	250
Dissolved solids, mg/l	760	230	1500
Suspended solids, mg/l	0	0	0

4.3 Characteristic of the soil samples

The physical properties and chemical constituents of the four soil samples SS1 - 4, collected from Muirungi, Kavutiri, Kimakia and Kiarutara locations respectively are presented in Table 4.3. The soils exhibited strong acidic pH, which is an indicator of potential presence of aluminium ions that are highly soluble in low pH. When the soil material pH is above 5, aluminium ions are precipitated out of the soil suspension and leached out. The pH will also influence the electrical conductivity (EC) because in acidic pH the hydrogen and hydroxyl ions will carry charges while cation exchange capacity (CEC) increases with reduction of pH that contribute to increased cations. Electrical conductivity is also dependent on clay/sand composition and organic matter present. Soil samples with large content of clay and less sandy materials have higher electrical conductivity.

Table 4.3. Characterisation of the soil samples

Sample Code	SS1	SS2	SS3	SS4
Sampled location	Kavutiri	Muirungi	Kiarutara C67 road	Kimakia Forest
Soil moisture status during collection	Dry	Dry	Moist	Moist
pH	4.36	4.24	4.84	4.55
EC (Salts) (uS/cm)	79.3	92.3	38.8	41.6
Phosphorus (ppm)	2.61	2.08	0.80	2.33
Potassium (ppm)	31.9	27.1	56.9	81.1
Calcium (ppm)	72.4	34.3	70.2	114
Magnesium (ppm)	18.6	9.44	10.8	20.3
Sodium (ppm)	8.54	17.5	12.4	7.86
C.E.C (meq/100g)	1.90	1.28	1.45	2.60
Organic Carbon (%)	3.08	3.61	4.74	3.05
Exchangeable aluminium (meq/100g)	1.49	1.45	0.35	1.39
Sand (%)	28.0	36.0	71.7	39.4
Silt (%)	8.00	18.0	24.0	16.0
Clay (%)	64.0	46.0	4.29	44.6

All the soils were found to have high concentrations of calcium and potassium but less of phosphorous, magnesium and sodium. The concentration of the minerals could have been influenced by the number of negatively charged sites available in the soil. Higher mineral concentrations are observed at higher cation exchange capacity (CEC) values because the negatively charged sites determine the number of cations attracted to the soil. In all soil samples, the organic carbon was found to be lower than the average 8% for most Ando soil samples which may be attributed to discarding of the top soil material before sampling.

The Sample SS1 from Kavutiri, Embu County, had the highest proportion of clay at 64% and least of sand at 28% compared to the 4.29- 46% clay and 36 -71.7% sand for the other soil samples. The greater proportion of clay and less of sand suggest for Sample SS1 would have better adsorption properties.

4.4 Bulk density of untreated soil sample

The average bulk densities of the soil samples ranged from 0.54 to 0.95 g/cm^3 (Table 4.4) consistent with density values of Ando soils lower than $0.9 g/cm^3$ and as low as $0.3 mg/m^3$. The low values indicate high porosity and organic matter presence in the soil. The soil low bulk density contributes to increased surface for adsorption.

Table 4.4. Ando soil bulk density

Sample code	Source	Average bulk density (g/cm^3)
SS1	Kavutiri	0.73
SS2	Muirungi	0.81
SS3	Kiarutara C67 road	0.54
SS4	Kimakia Forest	0.95

4.5 Fluoride adsorption by unbaked soil samples

All the four Ando soils samples applied at a dosage of 2 g per 50ml fluoride water of 7.1 mg/l initial concentration removed between 62 and 76% of fluoride from borehole water at 30 minutes contact time and 92 to 100% in 2 hours (Figure 4.1), which indicated a large potential for defluoridation. At 2 hours contact time, the soils achieved fluoride residues of non-detect,

0.4, 0.3 and 0.6 mg/L for the SS1, SS2, SS3, and SS4, respectively, which is below the WHO upper limit of 1.5mgF/l in drinking water.
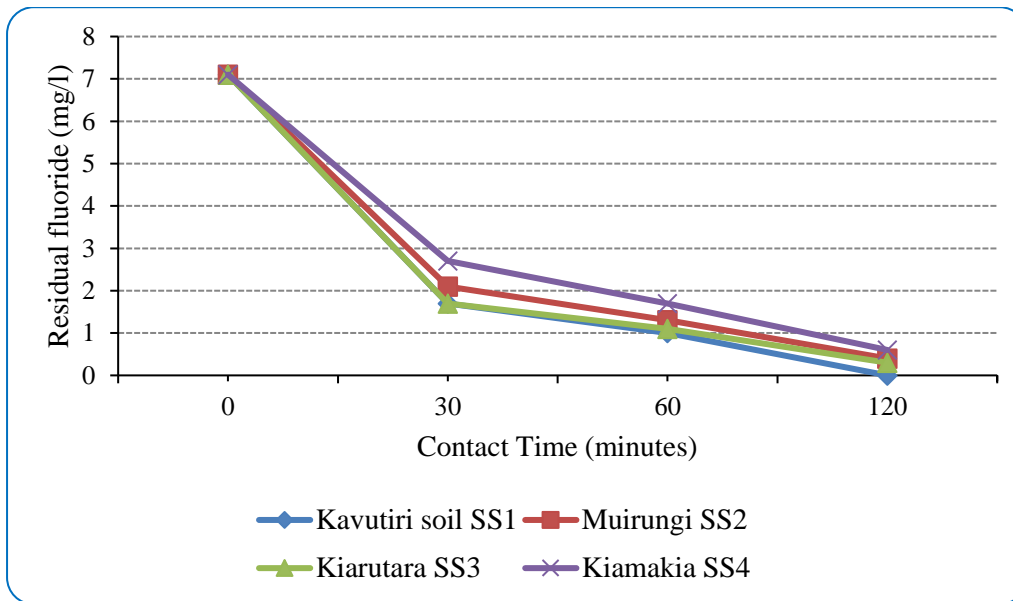
Figure 4.1. Fluoride removal from borehole water for soil samples from different location (initial fluoride 7.1 mg F^{-1}/l, mixture 2 g of Ando soil/ 50ml fluoride water)

Soil samples SS1 and SS3 exhibited similar and greater fluoride removal rates than the other two samples. The better performance of the SS1 sample may be attributed to its higher exchangeable aluminium and clay content when compared to the other soil samples. Aluminium has high potential of adsorbing fluoride ions because its ability to form stable complexes with fluoride. For example, Al^{3+} reacts with F- to form AlF_n^{3-n} where $0 \le n \le 6$ (Syuntaro Hiradate, 2004). The adsorption of fluoride by aluminium occurs either due to coordinated adsorption or creation of new adsorption sites as a result of broken bridge-connection between hydroxyl and aluminum ions in a complex adsorption mechanism. Aluminium concentration in solution is enhanced by acidic conditions and exhibits different species in soil material based on the pH. When the soil pH ≤ 4, the dominant aluminum ion is Al^{3+} while at pH >4 and above, $Al(OH)^{2+}$ and $Al(OH)_2^{+}$ species are formed due to hydrolysis. As the pH continue to increase, these species are precipitated as $Al(OH)_3^{0}$. Further increase in pH will lead to the amphoteric $Al(OH)_4^{-}$ species (Barnhisel and Bertsch, 1982; Thomas and Hargrove, 1984). Clay also has potential for adsorbing fluoride because of its composition with kaolinite, vermiculite and montmorillonite that have very strong adsorption capacity.

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Soil sample SS1 exhibited a greater proportion of clay and larger concentration of exchangeable aluminium than the other sample. It also exhibited a greater fluoride removal. Consequently, the sample SS1 was selected for the next phase of the study.

4.6 Changes in soil sample after calcination

Both the physical and chemical properties of the selected soil sample were assessed. During calcination, soil sample was observed to change colour and texture properties. Up to 200°C temperature, the soil colour was dark red but changed to light red at 300 up to 700°C. Similarly, the texture changed from sticky and to loose material due to increased sand-sized particles. These changes were attributed to expulsion of moisture and organic matter in the soil sample and possible changes in soil mineralogical composition.

Figure 4.2 shows the highest weight loss was observed between 0 and 100°C and the least at temperature between 600 and 700°C. At 100°C, free water was expelled from the soil. Between 100 to 280°C organic matter and other volatile substances were removed through endothermic process. Above 280°C, exothermic reactions took place, causing ignition of the organic matter (DeBano, 1991). At temperature between 500 and 600°C the weight loss could have been due to glowing combustion of organic matter while the chemically bound water was also removed from the soil material (DeBano, 1991). Between 600 to 700°C, the change of weight could have been due to irreversible removal of water that is structurally held by clay minerals (DeBano, 1991).
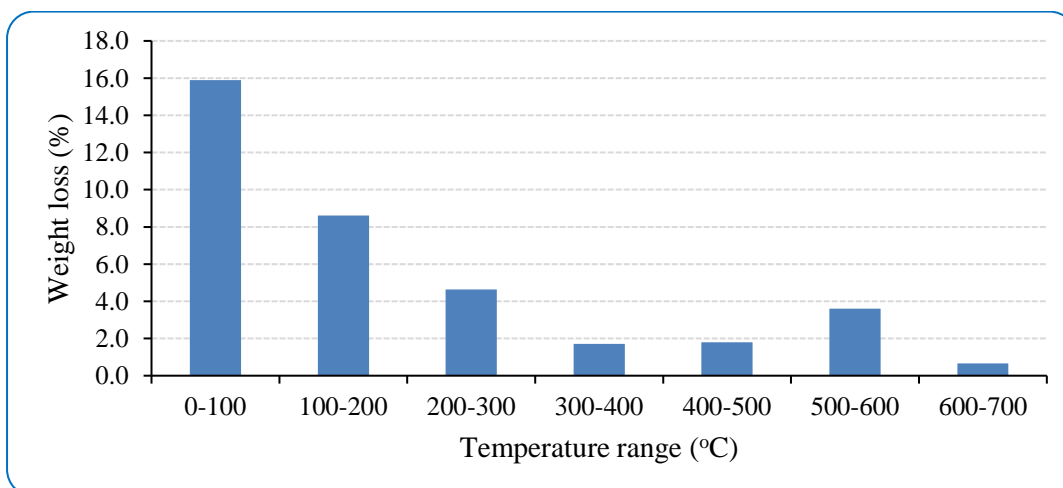
Figure 4.2. Weight loss of soil sample at different temperature ranges as a percentage of the original weight

The chemical changes occur when mineral elements are under extreme heat temperature. Nitrogen and sulphur get volatile at temperature range of 200 to 375°C (Hosking, 1938; Tiedemann, 1987) while potassium, phosphorous, manganese, magnesium and calcium compositions will only be affected by temperature above 700°C (Raison et al, 1985).

4.6.1 Chemical composition of the heat-treated soil sample

The results of x-ray fluorescence (XRF) analysis of untreated Ando soils and calcined at different temperatures (Figure 4.3 – 4.5) showed that the main elemental oxides that were significantly affected by heat were aluminium, silicon and iron which account for 97% of the soil mineral composition. While the overall proportion of aluminium increased with temperature, there was slight decline in silicon and iron proportions, which was attributed to molecular dissociation. Aluminium oxide increase could be attributed to the oxidation of exchangeable aluminium cations which were loosely held by the clay mineral and colloids. At low pH of less than 4.5, aluminium cations are predominant in the soil suspension after displacing other exchangeable metallic cations in the soil solution. When the soil loses water and organic matter which are responsible of maintaining the ions in the soil material, a portion of exchangeable aluminium ions become oxidized, which increases the amount of aluminium oxide (Fatubarin and Olojugba, 2014).
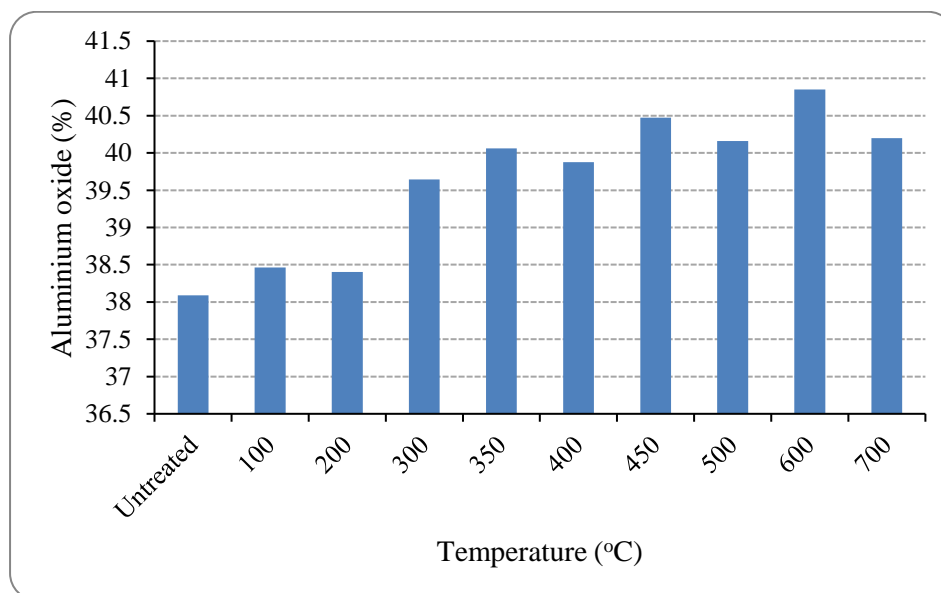
Figure 4.3. Changes of Aluminium concentration (%) content when soil is heated
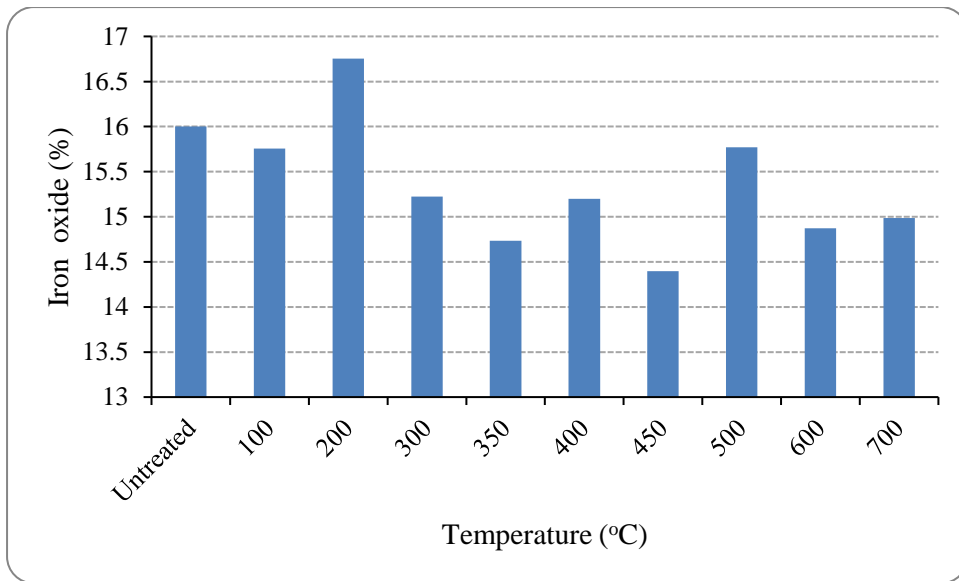
Figure 4.4. Changes in Iron concentration (%) when soil sample is heated
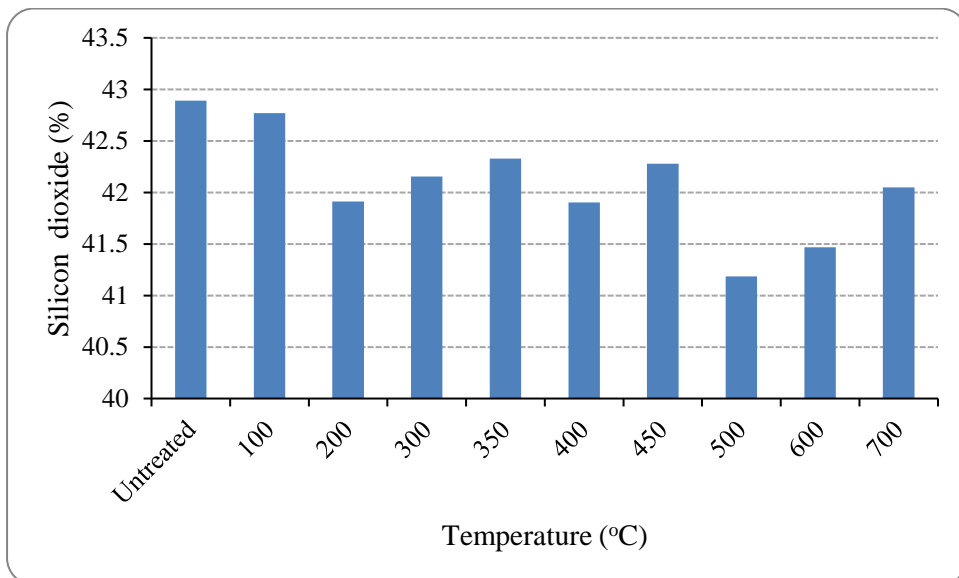
Figure 4.5. Changes in Silicon concentration (%) when the soil is heated

Analysis of crystalline structure of Ando soils with the x-ray diffraction (XRD) did not yield the high intensity sharp narrow peaks that characterize the crystalline structures. Instead, the diffraction peaks as shown in Figure 4.6 for the untreated soil sample and Figure 4.7 for soil heated at 350°C were not distinct. The lack of distinct diffraction peaks could be attributed to the non-crystalline aluminium and iron complexes in Ando soil.
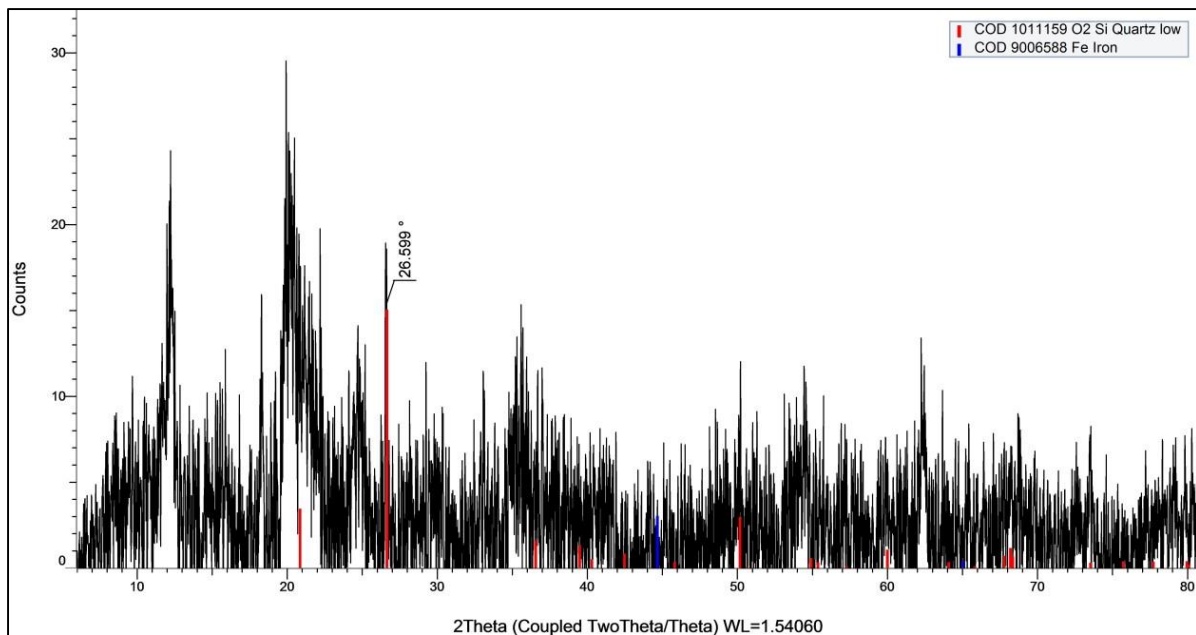
Figure 4.6. The XRD image of the unbaked soil sample
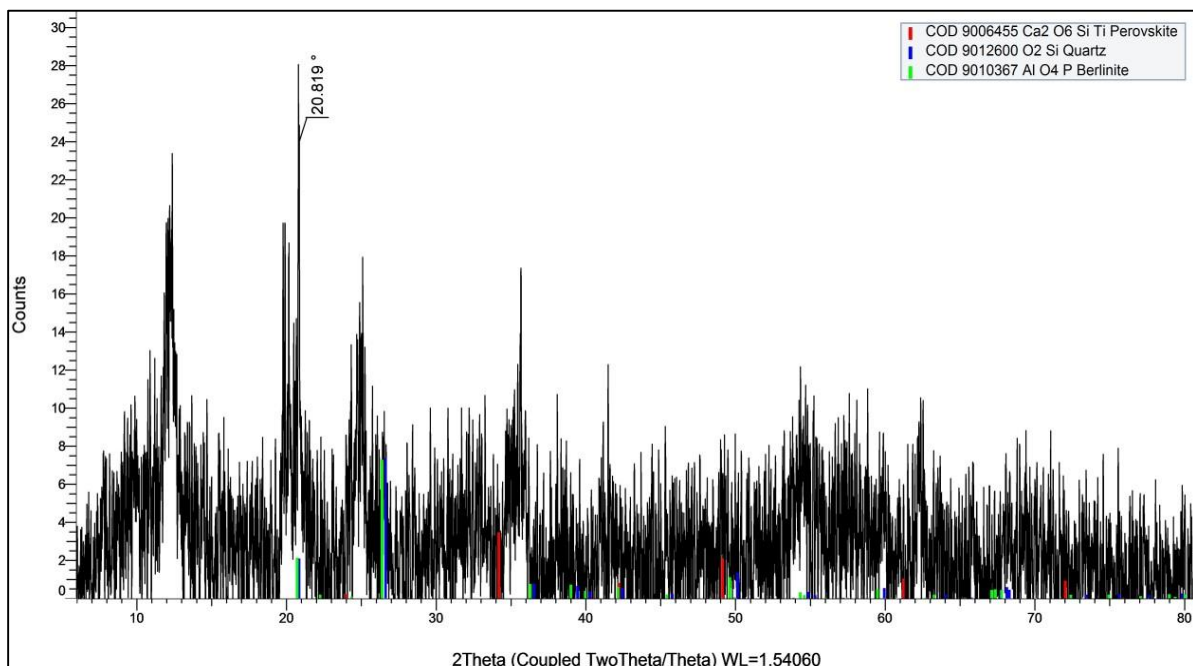
Figure 4.7. The XRD image of soil sample heated at 350ºC

4.7 Results of Fluoride adsorption tests

Fluoride adsorption tests were carried out for calcined and untreated Ando soil. The following sub-sections presents defluoridation results and discussions.

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4.7.1 Fluoride removal by Ando soil

Defluoridation of borehole and simulated fluoridated water using 2 g of calcined Ando soils calcined at 350°C in 50ml of fluoride water showed fluoride of 93% compared to 97% respectively at 30 minutes contact time (Figure 4.8). The residue fluoride concentration in borehole water was 0.5mg/l and 0.2mg/l in simulated fluoridated water from the initial concentration at 7.2mg/l which was within the allowable concentration in drinking by WHO of 1.5mg/l.

The 4% difference between the removal rate of borehole water and simulated fluoridated water was attributed to ion interference and marginal co-ions effect by the higher concentration of alkalinity, sulphates and chlorides compared to simulated fluoridated water. However, this difference in removal rate was not consistent with contact time and at 180 minutes where fluorides was not detected in both solutions.
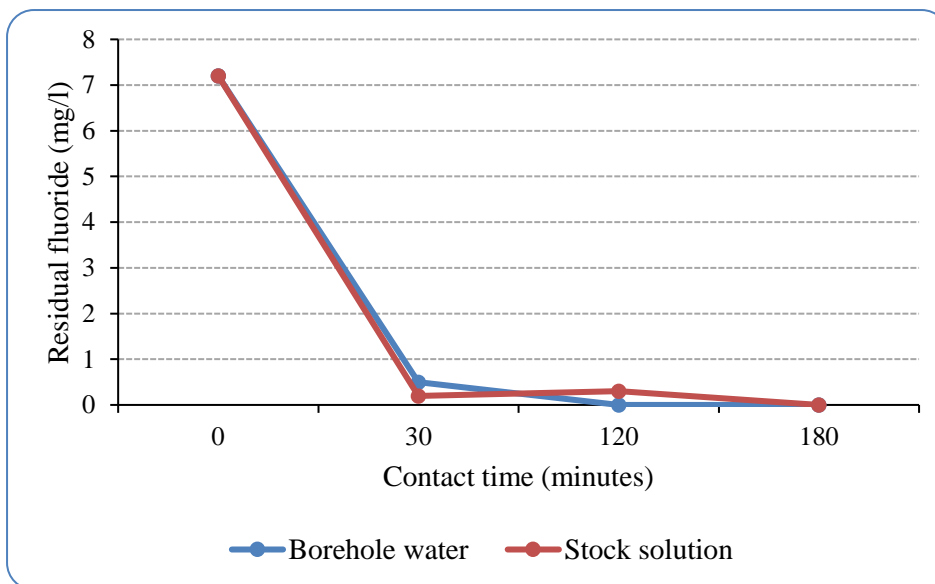
Figure 4.8. Fluoride removal from borehole and simulated fluoridated water for Ando soil sample baked at 350°C (initial fluoride concentration, 7.2 mg/L; volume, 50ml; adsorbent dose, 2 g; pH, 6.33; continuous agitation).

4.7.2 The effect of calcination on fluoride adsorption

Fluoride adsorption by Ando soil thermal treated at 100 to 700°C had varied results at 30 minutes contact time as depicted in Figure 4.9. The result shows a decline in fluoride adsorption between 100 to 200°C, and then improved fluoride removal between 200 to 400°C followed by

a decline up to 700ºC. Consistently higher adsorption by the calcined soil of up to 79% was observed for calcination temperature range of 300 to 450ºC.

Figure 4.9. Fluoride removal from borehole water for Ando soil samples baked at varied temperatures (300-500ºC) compared to unbaked sample (initial concentration, 7.1 mg/l; volume, 50ml; pH, 6.33; contact time, 30 minutes; adsorbent dose 2 g; intermittent agitation).

To refine the calcination temperature with the highest adsorption capacity, untreated and soil samples calcined at 300 to 500ºC were applied in fluoride adsorption over duration of 4 hours (Figure 4.10). Except for the sample calcined at 500ºC, all the Ando samples achieved fluoride removal rates of over 80% and achieving 90-93% within the 4 hr period. However, while the fluoride removal increased with time for calcined samples, there was decline of up to 15% for the untreated soil sample after 2 hours. Mbugua et al. (2020) attributed the reduction in fluoride removal by the untreated soil sample to steep concentration gradient between the liquid and the adsorbent, making fluoride ions that are loosely held, for example, by organic matter migrate back to the sorbate. However, the drop in fluoride adsorption could also be due to changes in the liquid pH influenced by the balance in charges during adsorption over long contact time. This change can create an opportunity for the hydroxide ions to become more active in competing with fluoride for the positively charged sites leading to the drop in fluoride adsorption. Whichever, the case, the result suggests some instability in the attachment

mechanism for the untreated soil and give credence to use of calcined to improvement of the Ando soil for fluoride removal by heat treatment.

The 350ºC soil samples achieved the highest fluoride removal within the first 30 minutes and maximum removal of 93% within at 3 hours.

In all cases, adsorption was rapid within the first 30 minutes and then gradual until equilibrium was reached. A maximum fluoride removal of 93% was achieved for the 350ºC soil samples which equilibrated at 3 hours. However, the removal was only marginally higher than that of the 300, 400 and 450 ºC which was achieved about 90-91%.
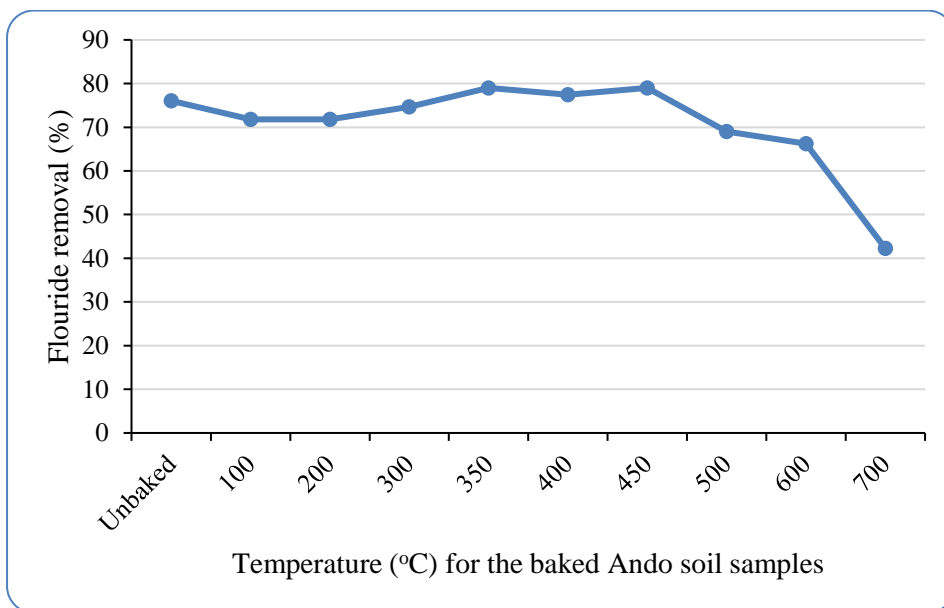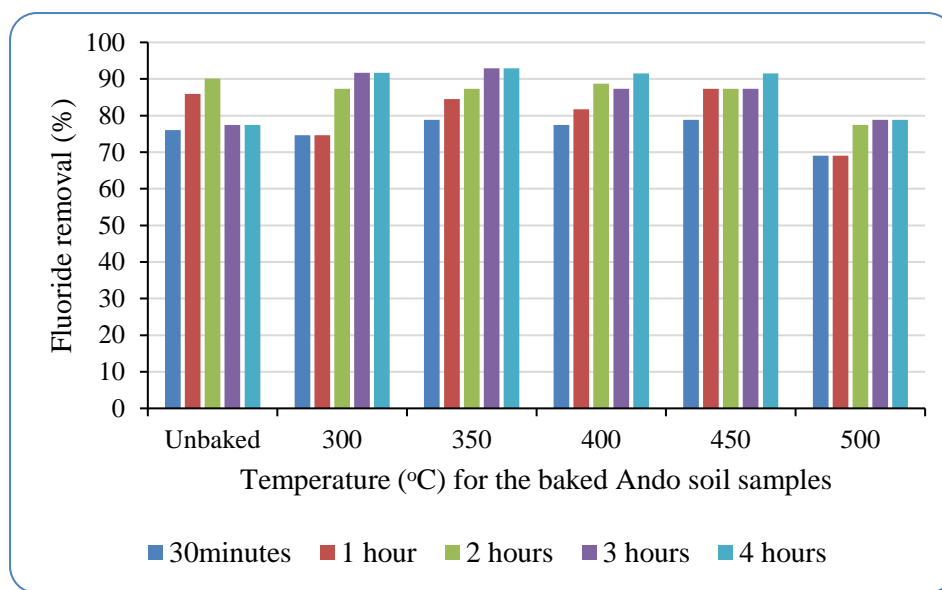

Figure 4.10. Percent fluoride removal from borehole water for Ando soil samples baked at temperatures of 300 to 500ºC compared to unbaked sample (initial concentration, 7.1 mg/l; volume, 50ml; pH, 6.33; adsorbent dose, 2 g; intermittent agitation).

Because the soil sample calcined at temperature 350ºC exhibited better adsorption rate relative to the other baked samples, 350ºC was considered the optimum calcination temperature and used for subsequent adsorption tests.

4.7.3 Effect of agitation on adsorption

Mixing of untreated soil with fluoride water resulted in a more turbid suspension compared to the calcined sample (Figures 4.11 and 4.12). The slow settlement and turbidity could probably be attributed to presence of organic matter and colloids as suspended solids which were reduced

in the thermal treated soil sample. The suspension obtained for the untreated soil indicates better material dispersion and could have enhanced increased surface contact between the adsorbent and adsorbate. On the other hand, quick settlement of the suspended material could have reduced the contact surface area during intermittent agitation. Therefore, agitation both continuous and intermittent was considered for the adsorption tests.
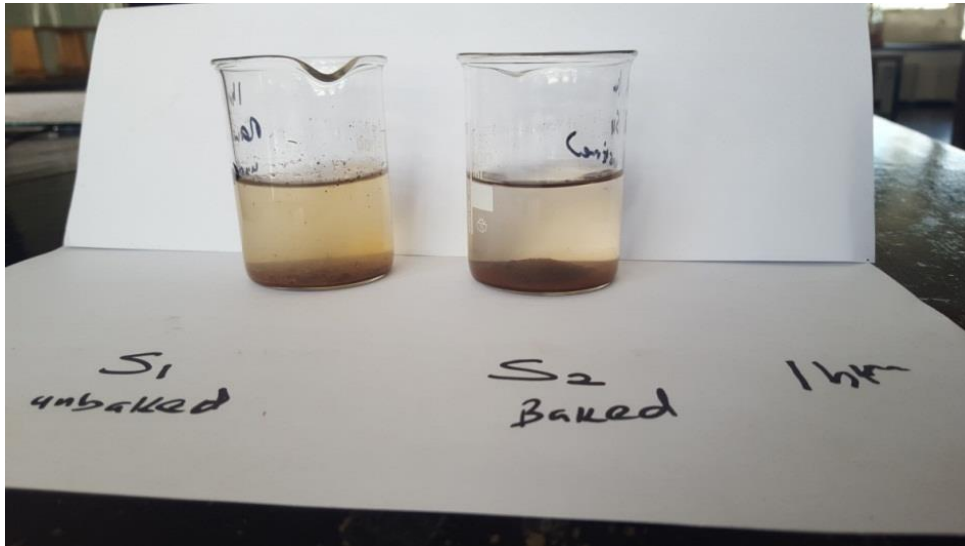
Figure 4.11. Turbidity in baked and unbaked soil sample suspension after 10 minutes settlement duration

Figure 4.12. Turbidity in baked and unbaked soil sample suspension after filtration.

Continuous agitation improved adsorption rate of fluoride in both adsorbent materials in low and high initial fluoride concentration water (Figure 4.13 and 4.14) compared to intermittent agitation. The effect of agitation was more significant for high initial fluoride concentration as compared to low concentration.

When different agitation speeds were applied, the maximum adsorption occurred at 300 rpm achieving 6.6 mg/l initial fluoride concentration of 7.2mg/l representing 93% fluoride removal rate as shown in Figure 4.15. It can therefore be concluded that the 300 rpm speed provides all the necessary agitation for contact and that higher speeds may interfere with the contact between fluoride ions and the exchange sites. This rotation speed was therefore maintained for adsorption mix subjected to continuous agitation.
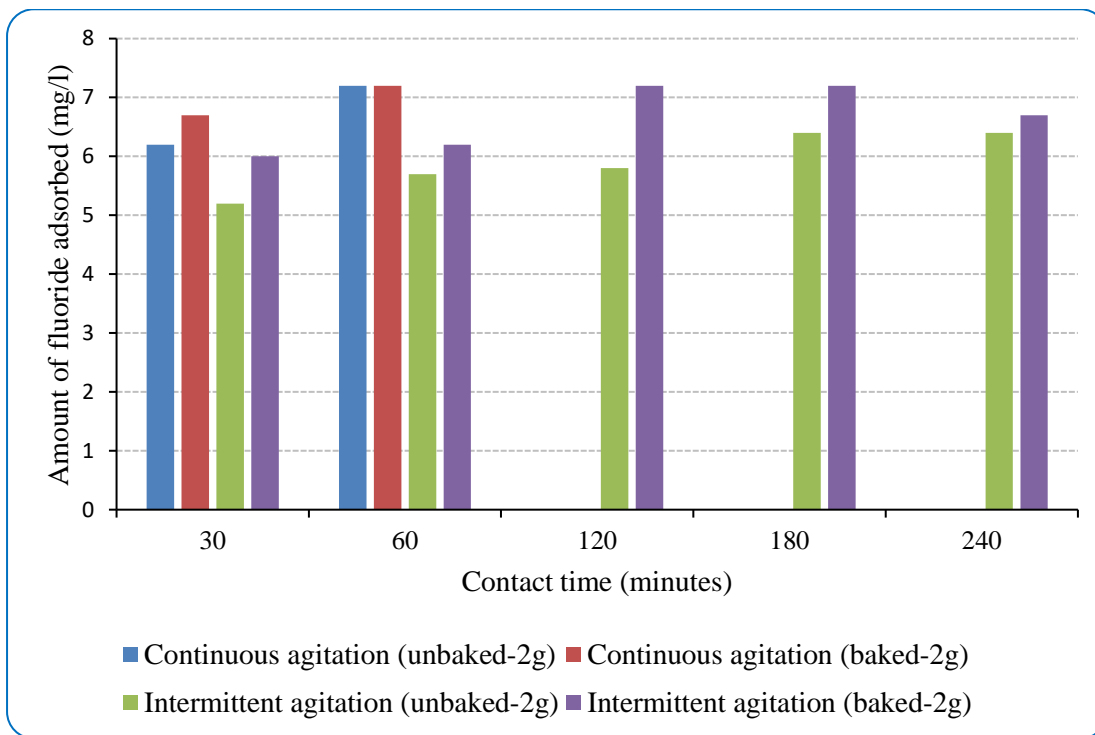
Figure 4.13. Amount of fluoride removed from borehole water for baked and unbaked Ando soil samples in continuous or intermittent agitation over different contact time. (initial fluoride concentration, 7.2 mg/l; volume, 50 ml; pH, 6.38; adsorbent dose, 2 g; agitation speed, 300 rpm; soil baked at 350ºC).
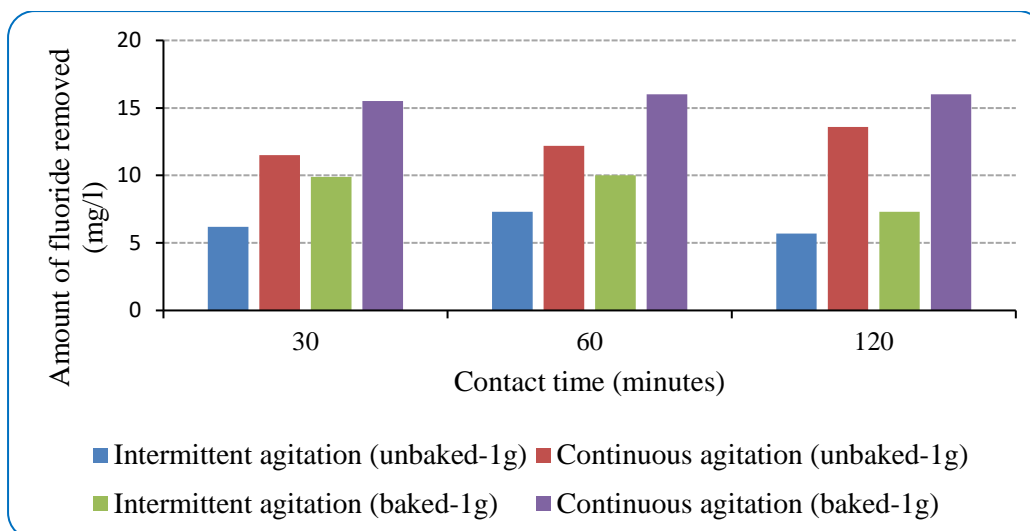
Figure 4.14. Amount of fluoride removed from borehole water for baked and unbaked Ando soil samples in continuous or intermittent agitation over different contact time. (initial fluoride concentration, 18 mg/l; volume, 50 ml; pH, 6.4; adsorbent dose, 1 g, agitation speed, 300 rpm; soil baked at 350°C)
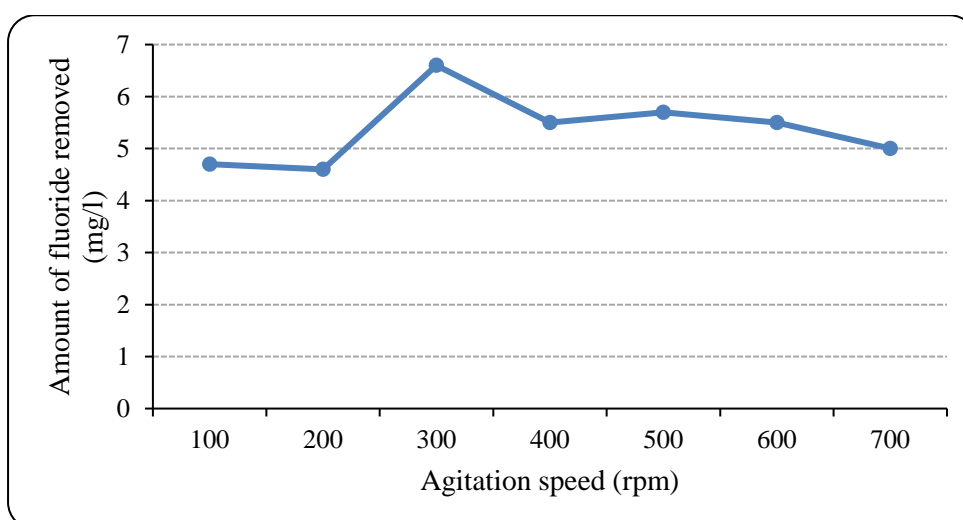
Figure 4.15. Amount of fluoride removed from borehole water for baked Ando soil sample at varied agitation speeds (initial concentration, 7.2 mg/l; volume, 50ml; pH, 6.58, adsorbent dose, 2 g; 30 minutes contact time; soil baked at 350°C).

4.7.4 Effect of pH on fluoride adsorption

Figure 4.16 shows the influence of pH on fluoride removal which indicates an increase in adsorption capacity at the region below the pH value 5.6 and a reduction when acidity in the

solution reduces. In both baked and unbaked Ando soil samples, there was similar trend in adsorption of fluoride from low to high pH values apart from variation at pH 8.5 when the adsorption capacity of unbaked soil sample was slightly higher probably due to availability of colloidal material in unbaked soil sample. The highest adsorption capacity achieved in borehole water with low fluoride concentrations was at the pH between 2 and 3.4 in borehole water (Figure 4.16) while in high fluoride concentrations in simulated fluoridated water, this was at the region between 2.06 -2.19 (Figure 4.17).

The increased fluoride adsorption at lower pH could be attributed to increased formation of positively charged sites that attracted the negatively charged fluoride ions in liquid through electrostatic force thus enhancing adsorption. At higher pH, there is decreased adsorption of fluoride probably due to reduced positively charged sites and also the hydroxide ions (OH^-) could be competing with fluoride ions for the limited active sites. The reduced adsorption of at very low pH could be due to disruption of adsorption sites by elevated acidity (Enos and Audre, 2019). The disruption leads to the release of iron and aluminium cations to the solution at low pH which bind with fluoride ions leading to fluoride complexes in the solution.
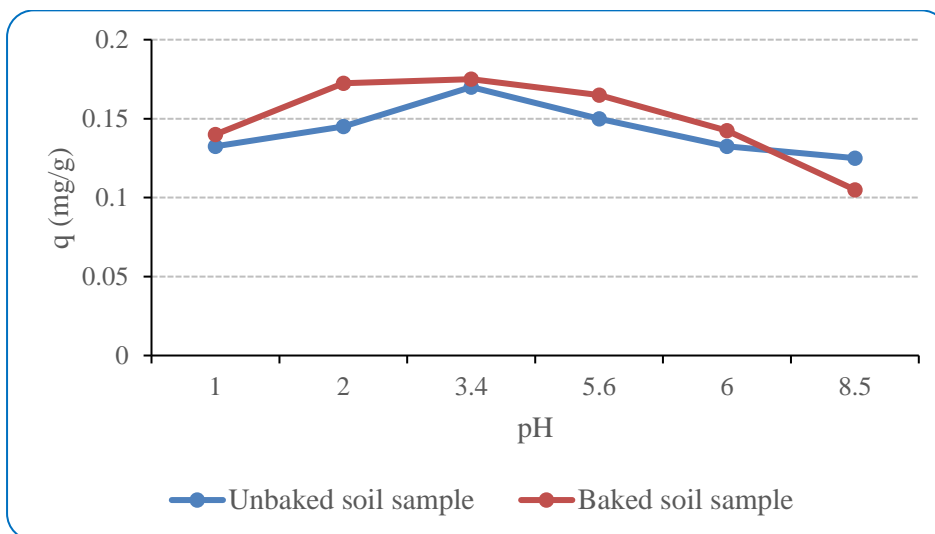
Figure 4.16. Percentage fluoride removed from borehole water for baked and unbaked Ando soil samples at different pH values (initial concentration, 7.1 mg/l; volume, 50ml; adsorbent dose, 2 g; contact time, 30 minutes; soil baked at 350°C)
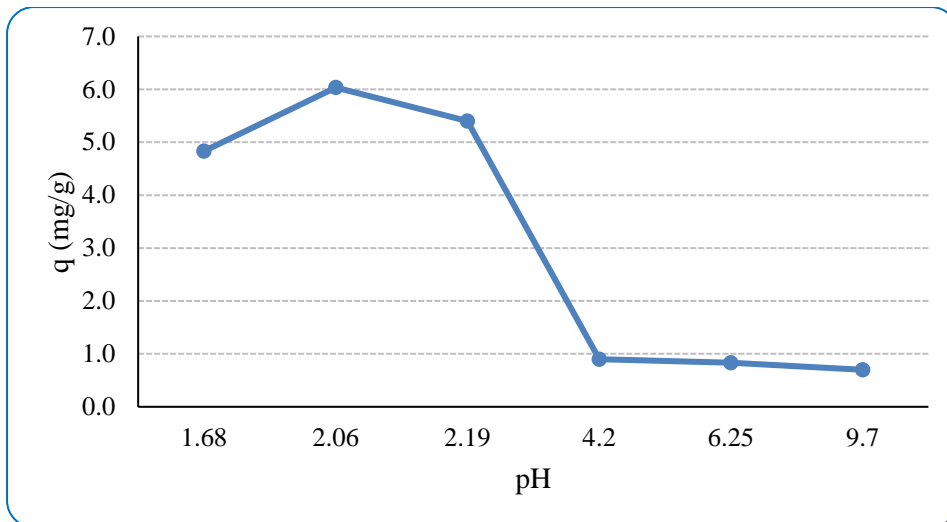
Figure 4.17. Percentage fluoride removed from simulated fluoride water for Ando soil sample at different pH (initial concentration, 19.5 mg/l; volume, 50ml; adsorbent dose, 0.15g; contact time, 30 minutes; soil baked at 350ºC)

4.7.5 The effect of contact time on fluoride adsorption

A rapid fluoride removal of 78.9% was noted to occur within the first 30 minutes of contact time in calcined Ando soil sample. Beyond 30 minutes, the rate of fluoride removal reduced before reaching equilibrium adsorption capacity of 93% in 3 hours (Figure 4.18).

Figure 4.18 Percentage fluoride removed from borehole water for baked and unbaked Ando soil samples at different contact time (initial concentration, 7.9 mg/l; volume, 50ml; pH, 6.33; adsorbent dose, 2 g; soil baked at 350ºC)

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On the other hand, the untreated soil had a similar pattern up to maximum fluoride adsorption capacity of 90% in 2 hours but dropped to 77% in 3 hours.

The rapid adsorption within the 30 minutes could be attributed to existence of multiple unoccupied sites for adsorption. As the contact duration increased, there was diminishing adsorption sites as well as reduced concentration gradient that slows down competition towards adsorption sites. The increased adsorption in the thermal treated adsorbent could be attributed to increased adsorption sites created by reduction of excess water and organic matter as well as the active aluminium ions.

The equilibrium contact time adopted for the calcined Ando soil adsorption was 3 hours.

4.7.6 The effect of adsorbent dose on adsorption efficiency

Overall, adsorption increased with increased amount of adsorbent dosage. Both treated and untreated samples had almost equal capacity of adsorption when intermittently stirred with only slight difference noticed at low and higher adsorbent dosage. At low dosage of up to 0.5 g/50 mlF⁻, thermal treated soil sample had up 7% difference in adsorption rate within 30 minutes compared to untreated soil sample. In contrast, as the dosage was increased to 2, 4 and 6 g/50 mlF⁻, the untreated soil sample exhibited better adsorption during the same contact time and the highest difference was observed 6.3% at 2 g/50 mlF⁻ (Figure 4.19).

Similar characteristics were also observed when the contact time was increased to 1hr. The treated soil sample had slightly higher adsorption rate compared to the treated soil sample at lower dosage of 0.5g and 4g as shown in Figure 4.20. However, at 1 g and 2 g, the treated soil sample adsorption capacity was slightly higher. At 6 g both soil samples had similar capacity during 1hr contact time duration. In both treated and untreated soil materials, the ideal dosage was reached at 4 g when the adsorption increase was minimal as the dosage was increased.

The thermal treated soil sample had slight advantage at lower quantity due to increased surface area for adsorption after heat treatment while for larger dosage, the untreated soil sample improved adsorption could be attributed to more suspended solids that took longer to settle thereby increasing contact duration.

At both 30 minutes and 60 minutes contact time, fluoride removal rate increases uniformly with dosage up to 4 g soil per 50ml and then declined sharply. Thus, the 4 g soil/50ml could represent the equilibrium dosage between the soil and the fluoride ions in solution.
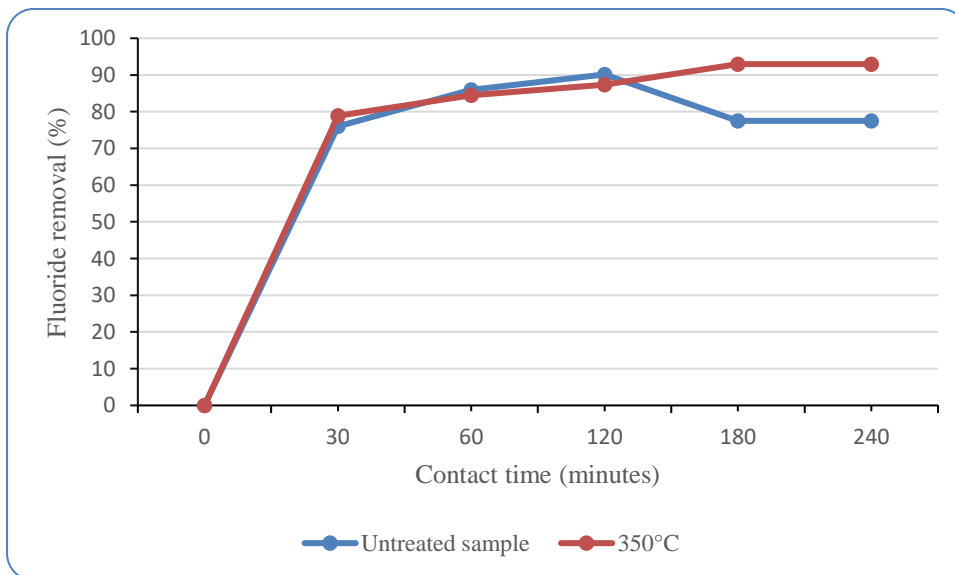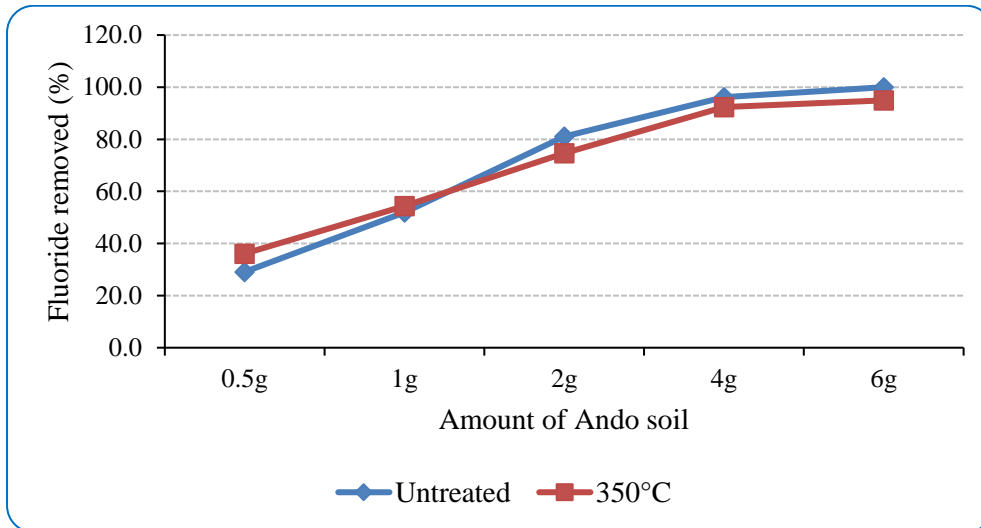

Figure 4.19. Percentage fluoride removed from borehole water for baked Ando soil samples at varied amounts (initial concentration, 7.9 mg/l; volume, 50ml; pH, 6.33; contact time, 30 minutes; soil baked at 350°C)
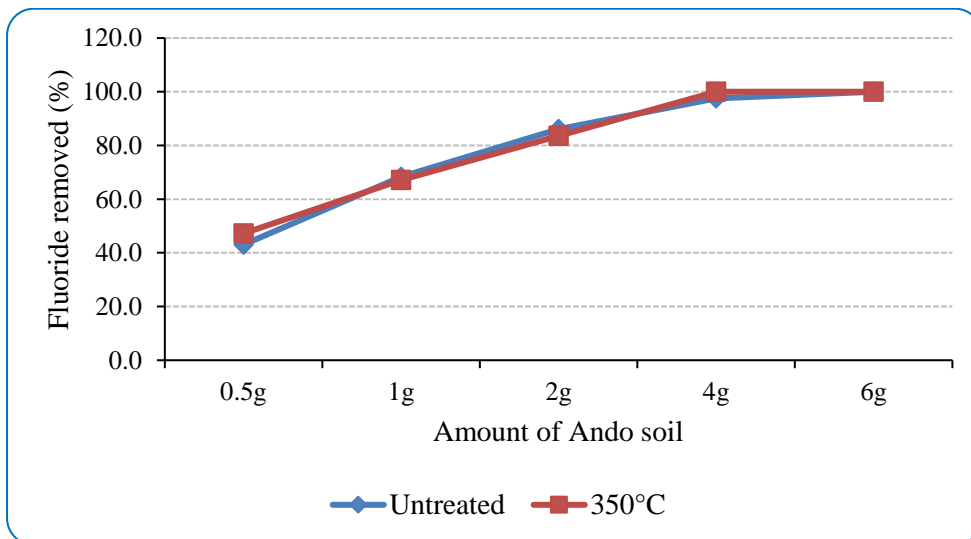
Figure 4.20. Percentage fluoride removed from borehole water for baked Ando soil samples at varied amounts (initial concentration, 7.9 mg/l; volume, 50ml; pH, 6.33; contact time, 60 minutes; soil baked at 350°C)

4.8 Fluoride adsorption isotherms

To establish equilibrium concentrations for determining adsorption capacity of the calcined Ando soil, adsorption tests were conducted with simulated fluoridated water of concentrations 5.8 to 16.9 mg/l. The percentage fluoride removal reduced with increase in fluoride concentration, which was attributed to exhaustion of adsorption sites (Figure 4.21). The data obtained was fitted to the Langmuir, Freundlich and Temkin adsorption isotherms in the following subsections.
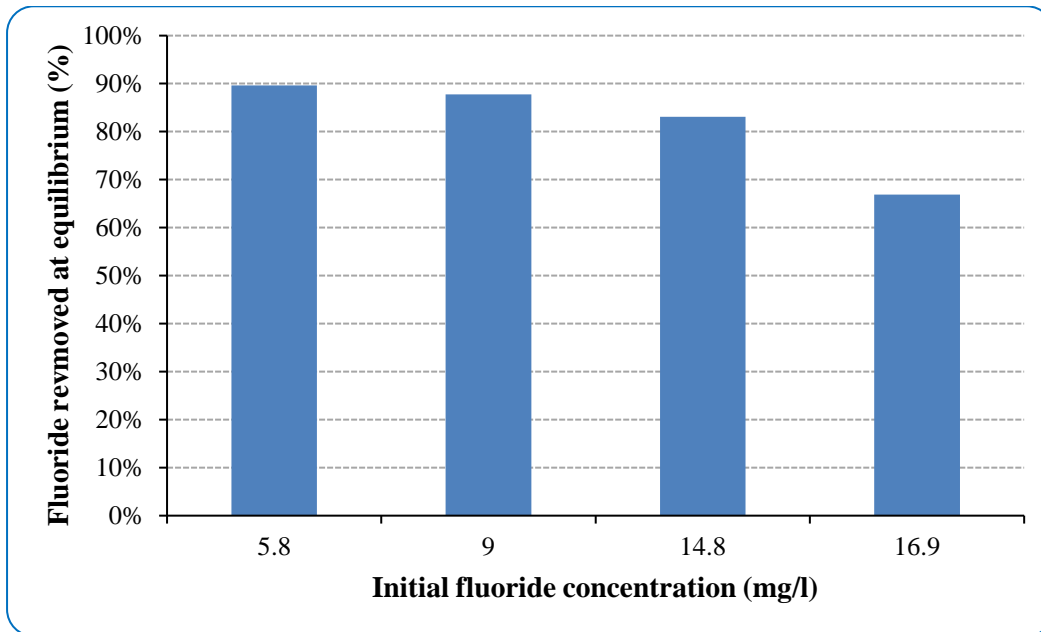
Figure 4.21: Baked Ando soil adsorption capacity in low to high fluoride range at equilibrium (pH, 2.06; contact time, 3 hours; continuous agitation; soil baked at 350°C)

4.8.1 Langmuir Isotherm

The adsorption capacity q_{max} was obtained as the reciprocal of slope of the linearized Langmuir plot $\frac{Ce}{qe} \, vs \, Ce$ (Langmuir 1 equation in table 2.1) in Figure 4.22 below. The study considered Langmuir 1 equation as it has been found to deviate marginally from the curve leading to better distribution of errors.

40
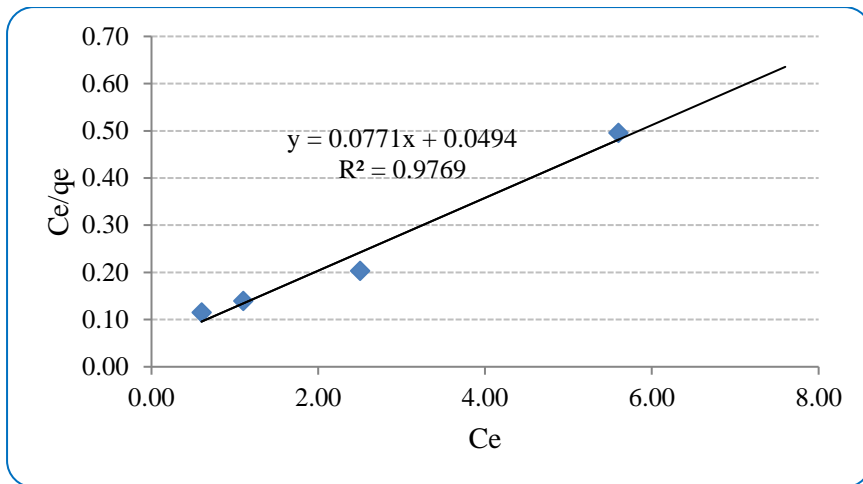
Figure 4.22. Langmuir plot for sorption of fluoride ions

4.8.2 Freundlich isotherm

Freundlich constants were obtained from a plot of *log qe* against *log Ce* (Figure 4.23) in which *n* is the reciprocal of the slope and ln KF is the y – intercept.
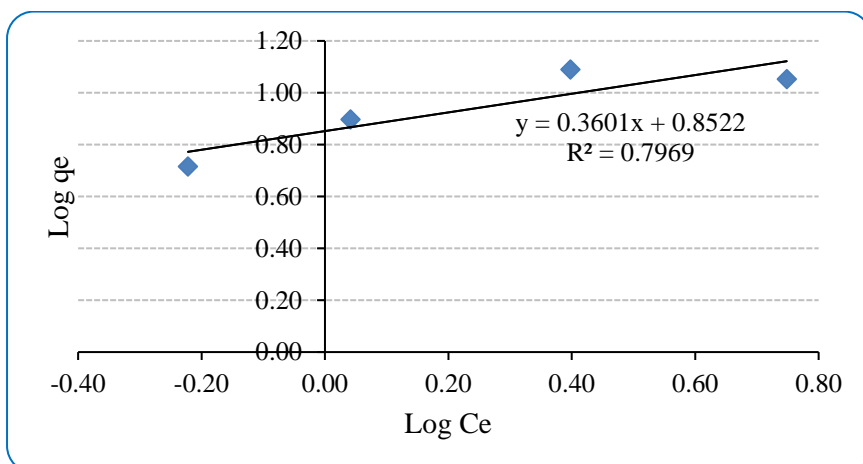
Figure 4.23. Freundlich plot for sorption of fluoride ions

4.8.3 Temkin isotherm

The Temkin isotherm constants were obtained by plotting the quantity sorbed qe against lnCe and the constants were determined from the slope and intercept (Figure 4.24). The constant bT is the slope while the AT is the exponential of (y-intercept/slope)
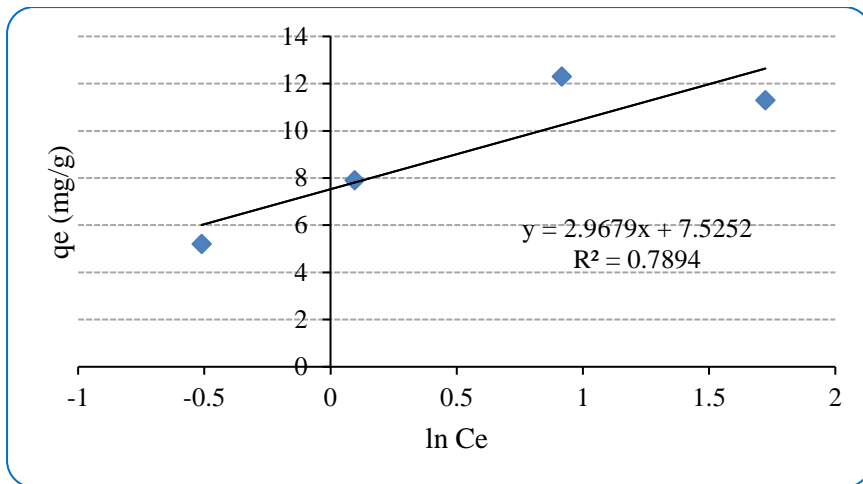
Figure 4.24. Temkin plot for sorption of fluoride ions

Comparing the data linear regression coefficient (R^2) for the three isotherm models, the adsorption of fluoride with Ando soils was best fitted with Langmuir model with an adsorption capacity q_{max} of baked Ando soil found to be 12.97 mg/g (Table 4.5). Langmuir isotherm indicates a homogenous adsorption material that could have been achieved by soil calcination.

Table 4.5. Summary of isotherm constants values

Isotherm	Langmuir			Freundlich			Temkin		
Parameter	R^2	b (L/mg)	q max (mg/g)	R^2	Kf	1/n	R^2	b_T	A_T
Isotherm value	0.9769	1.56	12.97	0.7969	7.12	2.78	0.7894	2.97	12.62

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study assessed adsorption of fluoride in borehole and simulated fluoridated water using calcined Ando soil. The following conclusions were drawn:

1. Baked Ando soil calcination temperature of 350°C applied at 2 g of calcined soil in 30 minutes reduced fluoride in 50ml borehole water from 93% from 7.1 to 0.5 mg/l, which was within WHO recommended concentration range of 0.5 to 1.5 mg/l in drinking water.

2. The maximum fluoride removal by calcined Ando soil was achieved at a calcination temperature of 350°C.

3. Calcination of Ando soil resulted in more stable adsorption of the fluoride during longer contact duration than the untreated soil and achieved 93% removal rate was achieved at 3 hours compared to 77% at 3 hours for the unbaked.

4. The study data fitted best to the Langmuir isotherm model with the highest linear regression coefficient of 0.9769 compared with 0.7969 and 0.7894 from Freundlich and Temkin, respectively indicating a homogenous adsorption material, and an adsorption capacity was 12.97 mg/g.

5.2 Recommendations

The recommendation of this study is to evaluate practical application of calcined Ando soil material in fluoride adsorption by conducting further research in the following areas.

1. Assess application of calcined Ando soil to remove fluoride from groundwater for household drinking water.

2. Future studies should evaluate regeneration of the heat-treated Ando soils media to assess potential for reuse in defluoridation.

3. The effect of calcined Ando soil on the taste of water treated by should be assessed.

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Appendix 1: Source of soil and water samples

Location	Type of sample	Sample Code	Southing	Easting
Kavutiri	Ando soil sample	SS1	0º 24' 40" S	37º 30' 14" E
Muirungi	Ando soil sample	SS2	0º 36' 19" S	36º 52' 24" E
Kiarutara C67 rd	Ando soil sample	SS3	0º 50' 06" S	36º 47' 15" E
Kimakia Forest	Ando soil sample	SS4	0º 48' 30" S	36º 46' 46" E
Naivasha Town borehole 1	Fluoride water sample	WP1	0º 42' 48" S	36º 26' 04" E
Naivasha Town borehole 2	Fluoride water sample	WP2	0º 42' 32" S	36º 25' 43" E
Naivasha Town shallow well	Fluoride water sample	WP3	0º 42' 43" S	36º 26' 01" E

Appendix 2: Fluoride adsorption by pristine soil samples

Soil sample collection sites	Contact time duration (mins)	Amount of residual fluoride (mg/l)	Dosage (g/50 mL)
Kavutiri	30	1.7	2
Kavutiri	60	1	2
Kavutiri	120	0	2
Muirungi	30	2.1	2
Muirungi	60	1.3	2
Muirungi	120	0.4	2
Kiarutara C67 road	30	1.7	2
Kiarutara C67 road	60	0.7	2
Kiarutara C67 road	120	0.3	2
Kimakia forest	30	2.7	2
Kimakia forest	60	1.7	2
Kimakia forest	120	0.6	2

Appendix 3: Calcined soil weight loss

Range of calcination temperature (°C)	Soil sample A weight (g)	Soil sample B weight (g)	Average weight loss (g)	Weight loss (%)
0-100	0.88	0.8	0.84	15.9%
100-200	0.51	0.4	0.455	8.6%
200-300	0.26	0.23	0.245	4.6%
300-400	0.1	0.08	0.09	1.7%
400-500	0.09	0.1	0.095	1.8%
500-600	0.2	0.18	0.19	3.6%
600-700	0.04	0.03	0.035	0.7%

Appendix 4: Soil bulk density

Sample code	Samples	Wet soil sample mass (g)	Mass of oven dried soil sample (g)	Moisture mass (g)	Bulk density (g/cm³)	Average bulk density (g/cm³)
SS1	Sample (a)	356.3	279.6	76.7	0.74	0.73
SS1	Sample (b)	343.59	266.03	77.56	0.71	
SS2	Sample (a)	473.96	318.26	155.7	0.84	0.81
SS2	Sample (b)	455.21	290.21	165	0.77	
SS3	Sample (a)	372.35	201.11	171.24	0.53	0.54
SS3	Sample (b)	376.85	206.7	170.15	0.55	
SS4	Sample (a)	532.17	367.67	164.5	0.97	0.95
SS4	Sample (b)	506.88	345.88	161	0.92	

Appendix 5: Soil XRF analysis for the major elements (%)

Soil sample	Al2O3 (%)	SiO2 (%)	Ti (%)	Fe (%)
Untreated	38.088	42.889	1.792	16.001
100°C calcined soil	38.464	42.768	1.738	15.758
200°C calcined soil	38.403	41.911	1.762	16.753
300°C calcined soil	39.646	42.155	1.612	15.223
350°C calcined soil	40.059	42.329	1.541	14.735
400°C calcined soil	39.877	41.903	1.625	15.199
450°C calcined soil	40.472	42.278	1.505	14.396
500°C calcined soil	40.161	41.186	1.614	15.771
600°C calcined soil	40.852	41.468	1.505	14.872
700°C calcined soil	40.198	42.048	1.528	14.985

Appendix -6: Untreated calcined soil XRD results

<u>Compound composition</u>
1 Quartz low O2 Si : 93.2 %

2 Iron Fe : 6.8 %
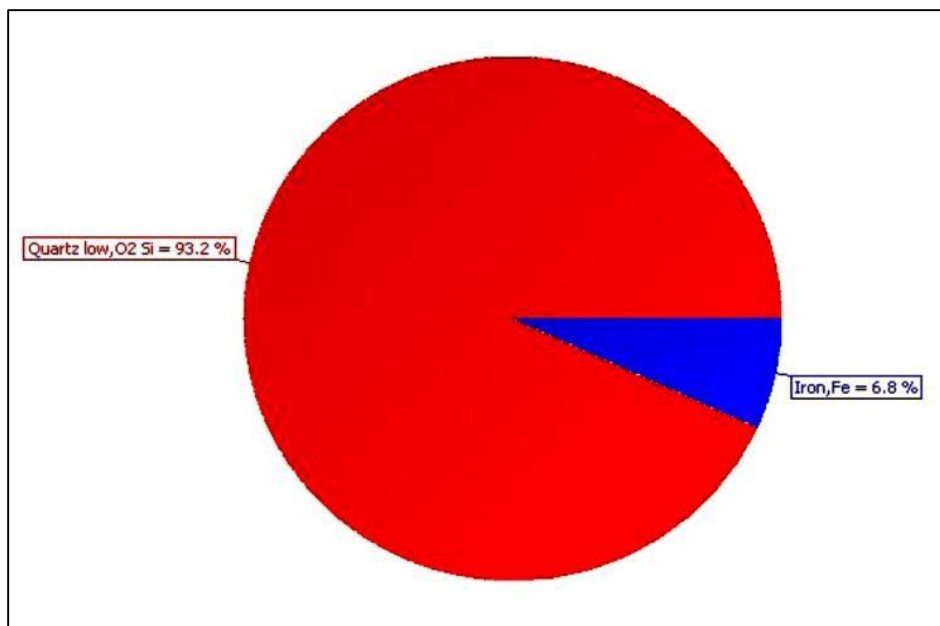
Appendix -7: 350ºC calcined soil XRD results

Compound composition
1. Perovskite Ca2 O6 Si Ti 23.3 %

2. Quartz O2 Si : 37.7 %

3. Berlinite Al O4 P : 39.0 %

Appendix -8: Study water samples fluoride concentration
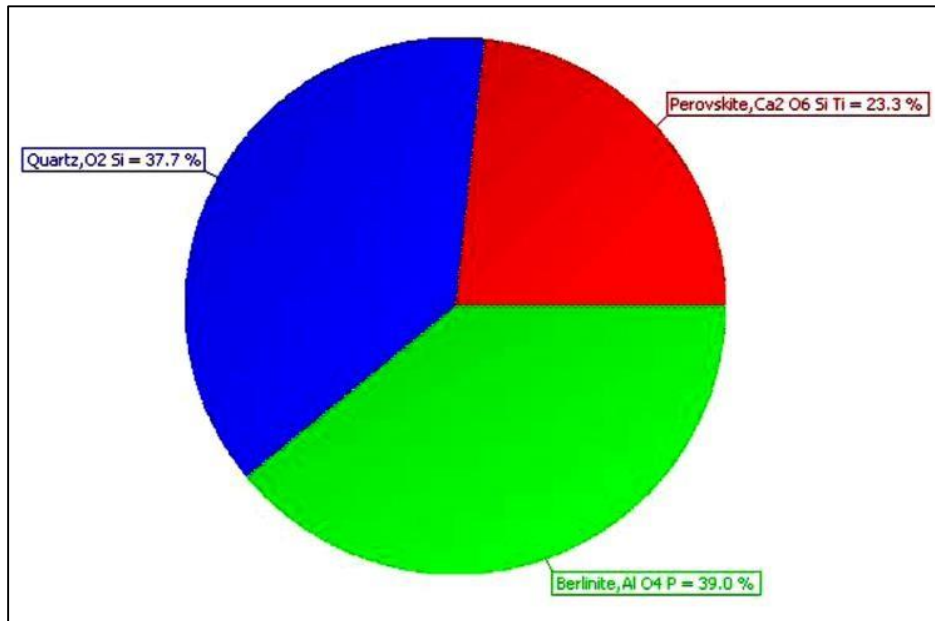
Source	Location	Samples collected	Fluoride concentration (mg/l)
Borehole BH1	Seasons Supermarket	BH1_S1	7.1
		BH1_S2	7.2
		BH1_S3	7.9
		BH1_S4	7.3
		BH1_S5	7.2
Borehole BH2	Rumax building	BH2_S1	5.7
Shallow well (SW)	Seasons Supermarket	SW_S1	5.5

Appendix -9: Fluoride adsorption for adjusted pH samples

	Untreated soil sample	350^0C calcined soil
pH level	**Fluoride removed by 2 g of soil sample (mg/l)**	**Fluoride removed by 2 g of soil sample (mg/l)**
3	16.8	18
4.5	15.6	17.9
6	15.3	18
7	14.4	17.6
8.6	13.3	16.3

Appendix -10: Fluoride adsorption by thermal treated and untreated Ando soil

	Contact time duration (minutes)				
Soil sample	**30**	**60**	**120**	**180**	**240**
Untreated sample	1.7	1	0.7	1.6	1.6
100°C calcined soil	2	1.7	1.6	1.8*	0.9*
200°C calcined soil	2	2.4	1.6	0.9*	0.3*
300°C calcined soil	1.8	1.8	0.9	0.6*	0.6*
350°C calcined soil	1.5	1.1	0.9	0.5	0.5
400°C calcined soil	1.6	1.3	0.8	0.9	0.6
450°C calcined soil	1.5	0.9	0.9	0.9	0.6
500°C calcined soil	2.2	2.2	1.6	1.5	1.5
600°C calcined soil	2.4	2.1	1.7	2.3	2
700°C calcined soil	4.1	3.4	3.5	3.9	4

Note:

- The initial fluoride concentration used for the tests above was 7.1 mg/l apart from those marked in asterisk
- Tests marked * had initial fluoride 7.2mg/l

Appendix -11: Fluoride adsorption results at varied contact time

Contact time	Residual fluoride concentrations (mg/l)			
	Untreated soil sample	350⁰c calcined soil	400⁰c calcined soil	450⁰c calcined soil
0 min	7.9	7.9	7.9	7.9
30 min	2	1.5	2.3	1.5
60 min	1.3	1.1	1.5	0.9
120 min	0.7	0.9	0.8	0.9
180 min	0	0.5	0.9	0.9
240 min		0.5	0.6	0.6

Appendix 12: Fluoride adsorption by varied adsorbent dose

Soil sample	Amount of soil in grams (dosage)	Residual fluoride concentration	
		30 minutes	60 minutes
Untreated soil sample	0.5	4.9	4.1
350°C calcined soil	0.5	4.6	3.8
Untreated soil sample	1	3.8	2.5
350°C calcined soil	1	3.6	2.6
Untreated soil sample	2	1.5	1.1
350°C calcined soil	2	2	1.3
Untreated soil sample	4	0.3	0.2
350°C calcined soil	4	0.6	0
Untreated soil sample	6	0	0
350°C calcined soil	6	0.4	0

Appendix 13: Fluoride adsorption at varied agitation

Contact time	Residual fluoride mg/l			
	Continuous stirring		Intermittent stirring	
	Untreated soil sample	350ºC calcined soil	Untreated soil sample	soil calcined at 350ºC
30 min	6.5	2.5	11.8	8.1
60 min	5.8	2	10.7	8
120 min	4.4	2	12.7*	11.1*
180 min	4.9*	2.1*		

Note:

- The initial fluoride concentration used for the tests above was 18 mg/l apart from those marked in asterisk

- Tests marked * had initial fluoride 18.4 mg/l