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DEFLUORIDATION OF GROUND WATERS USING INDIGENOUS CLAYS

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TABLE OF CONTENTS

Page

DEDICATION To MY PARENTS

HUSSEIN HAYATO, ELEMO KILTU, ROBA DADHI, T.BIRRU, ABBA JIFAR, HIYASU, FATUMA GUYYE, RISKO AHMED, HIKIMAT EFA, BAROO TUMISA, ALI BIRRA, AHMED ALAHAD, BAKALA DAWANO MOHAMMED AMIN, GUTAMA HAWAS, NADHI GAMADA, BURUSO BORU, BILAL AHMED, AND OTHER MARTYRS.

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LIST OF TABLES

LIST OF FIGURES

Figure Page

ABSTRACT

The properties of fluorine, its occurrence in nature and its source of incidence in various media were presented. The fluoride metabolism, absorption, distribution, excretion and its effect on living organisms were briefly reviewed. Several methods suggested from time to time for a defluoridation purpose were clearly stated. The fluoride content of natural waters collected from different parts of Ethiopia were reported. A study on the defluoridation of water (artificial and natural) by adsorption/ion-exchange with clays, collected from different parts of the country was examined. The effects of several parameters such as mass of adsorbent, contact time, volume of water, and pH of the solution on the fluoride removal efficiency of clays were studied. Among the adopted clays for defluoridation study, fired clay was found to be the least defluoridating agent. The other raw clays manifested the promising results to use at community and household levels with black and red clays being the best defluoridating agent. A mechanism of defluoridation by clays was verified experimentally. The regeneration capacity of the clays was tested using a regenerant 1 % (w/v) NaOH.

1. INTRODUCTION

Fluorine, is in group W A of periodic table. The electronic configuration of the fluorine is $1s^22s^22p^5$. The tendency to complete the outer shell with noble gas arrangement is the driving force for the extreme chemical reactivity of fluorine. Thus, it is the most electronegative element which has a high electron affinity and is unusually reactive. It reacts directly and very easily with nearly all elements, except for nitrogen, oxygen, and the lighter noble gases such as He, Ne, and Ar.

Fluorine is a slightly green gas with a penetrating odor. It is highly caustic (fluorine is extremely poisonous and, among other things, burns the skin). Liquid fluorine is pale yellow.

The metallic elements react with fluorine to form non-volatile ionic fluorides both in solution and in the crystalline state whereas the non-metallic elements react with fluorine to form volatile covalent compounds. In addition to the binary fluorides, a very large number of complex fluorides have been isolated, often with a fluoroanion containing a central atom of high oxidation number. Fluoride ions have a strong tendency to form complexes with various metal ions in aqueous solutions, e.g., AlF_6^{3-}, FeF_6^{3-}, ThF_6^{2-}, ZrF_6^{2-}, etc. [1, 2].

2. SOURCES AND METABOLISM OF FLUORIDE

2.1. Sources of Fluoride

The fluoride is found within various media in the form of compound. Its most occurrence is prevalent in rocks, soils, waters, foods, air, industrial byproducts, etc. The prevalence of fluoride in various sources boost human exposure to it.

The small amounts of fluoride minerals that occur in many industrial materials may eventually become an added source of fluoride. References are made to those materials that are processed thermally or chemically, such as limestone, cement, rocks, clays, shales, and metallic ores. Much of the fluoride is released during such operations as a secondary product.

The principal sources of fluoride available to man are drinking water, food, dings (including dentifrices, mouth washes, etc.), and airborne dusts and industrial contaminants [2, 5].

2.1.1. Fluoride in Rocks and Soils

Fluorine, being the most electronegative element, is so highly reactive that it is never encountered in its elemental gaseous form except in some industrial processes, but in the combined form. Fluorine is widely distributed in nature and occurs in continental rocks of the earth's crust to the extent of about 0.065 percent by weight. Among the elements, fluorine is about 13th in abundance. Its abundance is nearly as plentiful as carbon, chlorine, or nitrogen, but much more plentiful than copper, zinc, and lead. The minerals containing fluorine are found in both sedimentary and igneous rocks. Minerals containing fluorine can be categorized into three groups:

A. Fluorine rich minerals such as cryolite (Na_3AlF_6), 54.3%, and fluorite and/or fluorspar, CaF_2 (48.7%).

B. Minerals low in fluorine content such as fluorapatite, $CaF_2.Ca_3(PO_4)_2$ (3-4 %).

C. A miscellaneous group of minerals of varying fluorine content such as villiaumite (NaF), sellaite (MgF_2), nocerite ($Ca_3Mg_3O_2F_8$), fluellite ($AlF_3.H_2O$), and lepidolite, amblygonite, topaz, and bastnaesite.

The fluoride ion, has a single negative charge and a radius of 1.33 Å. In many minerals, fluoride substitutes for hydroxyl ion (OH^-) with 1.40 Å radius. Thus, fluoride is widely distributed in the lithosphere and hydrosphere. In average sea water the concentration of fluoride is about 1.3 mg L^{-1}; however, the activity of fluoride in the sea water is reduced significantly as a results of complexing. Even with correction for complexes, the activity of fluoride in sea water exceeds the activity of hydroxyl (OH^-) ions, illustrating the importance of the fluoride ion in regard to biological activity and inorganic precipitates although the concentration appears small. In most rivers and lakes; however, fluoride concentration is less than 1 mg L^{-1}. Fluoride is present in nearly all igneous and metamorphic rocks where it substitutes for hydroxyls in mineral structures, mostly in apatite, mica, and amphiboles [4, 6].

2.1.2. Fluoride in Water

Fluorides are present in nearly all potable waters owing to the solvent action of water on rocks and soil. A very small portion of the fluoride in drinking water enters directly from the sea or from atmospheric contamination, fluorides being present in coal, smoke, and volcanic steam [7, 8-9].

Trace of fluorides occur in many waters and higher concentrations are often associated with underground sources. In areas that are rich in fluoride containing minerals, e.g., fluorapatite, well waters may contain up to about 10 mg L^{-1} of fluoride per litre or even more. The highest natural level reported is 2800 mg L^{-1} [2, 8]. Most waters contain below 1 mg L^{-1} of fluoride. Occasionally, fluorides may enter a river as a result of industrial discharges. The natural concentration of fluoride in ground water depends on such factors as the geological, chemical, and physical characteristics of the water supplying area, the consistency of soil, the porosity of rocks, the pH, the temperature of interaction between rock and water. Surface waters are generally low in fluorides ($\leq$ 1 mg L^{-1}), while underground or subsoil waters, which have a greater opportunity to contact fluorine bearing rocks, usually contain higher levels of fluoride.

2.1.3. Fluoride in Food

Virtually all foodstuffs contain at least traces of the element. All vegetations contain some fluoride, which is absorbed from soil and water. Some foods may contain high levels, particularly fish, some vegetables, and tea. For instance, the fluoride content of some fish can be as high as 100 mg/kg, and tea may contain more than twice that concentration, in contrast to most of other foodstuff, which rarely exceed 10 mg/kg. The use of fluoridated water in food processing plants can often double the level of fluoride in prepared foodstuffs. Although the quantity of fluoride absorbed by the body is usually more closely related to the amount in drinking water than to the amount contained in diet, in some local situations the reverse may be true for instance, when there is a high consumption of sea fish [2, 8-9].

2.1.4. Fluoride in Air

Fluorine containing compounds are present in the air, mostly arising from industrial emissions. Concentrations of fluorine in air will vary depending on the type of industrial activity.

The sources of atmospheric fluorides include the burning of soft coal and the manufacturing of superphosphate, aluminum, steel, lead, copper, and nickel. Traces of fluoride in the air of rular communities and cities arise from both natural sources and human activity. Natural sources of fluoride including volcanic activity, in the air dust from soils, and sea water droplets, carried up into the atmosphere by winds. However, most of the airborne fluoride in the vicinity of urbanized areas is generated through human activities including aluminum industry, steel production plants, superphosphate plants, ceramic factories, coal burning power plants, brick works, glass works, and oil refineries [2, 9].

Atmospheric dust contributions are not considered significantly in Ethiopia; however, in many of these industries airborne fluorides from dusts and gases are potential health problem in several parts of the world, as the fluoride ions are completely absorbed from the lung [2, 8].

2.1.5. Fluoride in Others

Fluorides are also available to man in the form of drugs-either through specifically designed to liberate the fluoride ion in the body or those administered for other purposes, in which case the fluorine is usually covalently bonded and therefore, physiologically inactive. Various products such as toothpaste, tooth powders, mouthwashes, chewing gum, vitamin supplements, and drugs, may contain added quantities of soluble fluoride, mostly in inorganic form. Fluoride tablets have proved to be only partially successful in controlling caries. In one research project, young adults who took a daily tablet containing 1 mg L^{-1} of NaF were found to excrete 10 % of the fluorine in the faeces and 61.7 % in the urine. The remaining 28.3 % presumably found its way into the skeleton, soft tissues, and body fluorides. With children, a higher proportion (up to 72 %) of the absorbed fluoride is retained in the body [2, 8-10].

Fluoridated toothpaste have been used for two decades; they usually contain 1 mg of fluoride per g of toothpaste. These dentifrices do not consistently alter the fluoride content of the urine, but a small amount may be retained by the dental enamel and fluoridated chewing gum and mouthwashes, too [8].

2.2. Metabolism of Fluoride

The role of fluoride in human or animal metabolism is not known in detail. From the information available, it may be concluded that a certain quantity of fluorine is essential for the formation of caries-resistant dental enamel and for the normal process of mineralization in hard tissues. The element is metabolized from both electrovalent and covalent compounds. Low fluoride concentration stabilizes the skeletal system by increasing the size of the apatite crystals and reducing their solubility. The great affinity of fluorine for calcium phosphate is perhaps the most important from the physiological point of view. It results in accumulation in all tissues exhibiting physiological or pathological calcification. About 95 % of the fluoride in the body is deposited in the hard tissues and it continues to be deposited in calcified structures even after other bone constituents (calcium, phosphorus, magnesium, carbonate, and citrate) have reached a steady state. Age is also a decisive factor in deciding to what extent fluorine is incorporated into the skeletal. A pattern similar to that in bone is followed in the fluoride concentration in teeth. The uptake almost ceases in dental enamel after the age of about 30 years [8-11].

2.2.1. Absorption of Fluoride

Fluoride ingested with water is almost completely absorbed; however, fluoride in the diet is not as completely absorbed as from water, but the absorption is still substantial, although in the case of certain foods (e.g., fish and some meats) only about 25 % of the fluorides may be absorbed. Fluorides are absorbed from the gastrointestinal tract, the lungs, and the skin. The gastrointestinal tract is the major site of absorption. The extent to which the inorganic fluorides are absorbed depends on their solubility. The absorption of soluble fluorides such as NaF, by the gastrointestinal tract are rapid and nearly complete, whereas fluorides from insoluble or sparingly soluble compounds such as CaF_2, cryolite and the fluoride found in bone meal (fluoroapatite) are poorly absorbed. Absorption takes place both through the gastric membranes and through the intestinal tract by the normal process of diffusion. Certain dietary cations (e.g., calcium and iron) retard absorption of fluoride ion by forming low-solubility complexes in the gastrointestinal tract or if the diet contains high proportions of calcium, magnesium, aluminum, or iron complex fluoride ions of low solubility may be formed. In these circumstances, the faecal excretion of fluoride increases and the absorption decreases. As fluoride absorption from sodium fluorophosphate (Na_2PO_4F) is less influenced by the presence of calcium ions, it has been suggested that this compound may be more suitable than NaF in the manufacture of fluoridated salt. With sodium fluoride, the fluoride absorption may be reduced by the presence of foods rich in calcium. The second most common routine of absorption is through the lungs. Pulmonary inhalation of fluoride present in dusts and gases constitutes the major absorption of fluoride through the lungs. The last, and relatively rare, route of absorption is through the skin. Traditional milk feed up of children in some parts of the world may reduce the absorption of fluoride [2, 8-11].

2.2.2. Distribution of Fluoride

Absorbed fluoride is distributed throughout the body. It has been detected in all organs and tissues examined. It is evident that it is concentrated in tissues such as bones, thyroid gland, aorta, and perhaps the kidney. However, it is retained mostly in the skeleton, and small portion is retained in the teeth. The amount of fluoride present in bone depends on the fluoride intake, age, bone type, and the specific parts of the bone. In young animals fluoride is stored more in growing bone than older ones, trabular bone contains more fluoride than compact one, and the peripheral (biological active) surfaces of the bone take up fluoride more readily than the interior surfaces. The amount of fluoride in bone increases up to the age of 55 years. No matter how little the fluoride is ingested up to about half of the total quantity is incorporated in hard tissues. The mode of incorporation appear to be with one of two processes:

- by exchange, the fluoride ion replacing other ions or groups in the hydroxyapatite crystallites without seriously disrupting the apatite structures; and

- by accretion during crystal growth. These two processes are believed to occur at maximum rates during bone growth and tooth development.

The incorporation of fluorides in teeth may occur in three stages:

- during formation, when the fluoride is probably taken up uniformly throughout the tissues;
- during mineralization, when the uptake is greatest in the areas in which mineralization is actually taking place; and
- in the post mineralization period when the teeth are completely formed, the uptake is being confined to marginal regions of both the enamel and the dental [8, 9].

2.2.3. Excretion of Fluoride

The excretion of fluorides from the body is of great significance as prolonged exposure to excessive quantities is harmful. Fluorides are excreted through the faeces, sweet, urine, and other body fluids. However, the major route of fluoride excretion is through the kidney although it can also be excreted in small amount through the sweet glands, the lactating breast, and the gastrointestinal tract. Depending up on the diet the faecal excretion accounts for 10-30 % of the daily intake. Sweating may account for as much as 50 % of the total fluorides excreted in hot climate. Urine usually accounts for major excretion of fluorides. Fluorides appear rapidly in urine after ingestion and generally the level reflects the daily intake.

The excretion is influenced by a number of factors, including the general health of the person and his previous history of fluoride exposure; the rate of retention decreases with age and most adults can be regarded for practical purposes as " in balance". Under this steady state condition, the fluoride present in the body is sequestered in calcified tissues; most of the remain is present in plasma and thus available for excretion. Skeletal sequestration and renal excretion are the two major ways by which the body prevents the accumulation of toxic amounts of the fluoride ions. Traces may also be lost in milk, saliva, hair, and tears though it is probably not exhaled in the breath. Although fluorine is a natural constituent of human milk, the proportion of the daily intake secreted in the milk is negligible. Likewise the fluorine content of saliva is similar to that of blood but the loss of fluorine from the body by this route obvisouly very small indeed. However, the small amount present in the saliva may be of importance in the accumulation of fluorides in the surface enamel of the teeth [2, 9-11].

3. EFFECTS OF FLUORIDE ON LIVING THINGS

3.1. Beneficial Effects

A small dose of fluoride is incorporated into the hydroxyapatite of teeth which helps to reduce the solubility of the enamel under acidic conditions and thus, provides protection against caries. Fluoride has been fairly conclusively demonstrated to be an essential element for some animal species; in particular, fertility and growth rate are improved as a result of relatively small doses of fluoride [8-11].

3.1.1. Effects on Man

3.1.1.1. Fluorides in Teeth

The concentration of fluoride in teeth follows a similar pattern to that in bone. The age of the individual and the fluoride intake in food and water are the main factors. But in dental enamel, which has no cells and no circulation, the uptake almost ceases after the age of about 30 years.The mechanism by which fluorides give protection against dental caries is not yet settled. The two most likely theories at present are: that the presence of fluoride reduces the solubility of the enamel in acid; and that fluorides inhibit the activity of the bacterial enzymes that produce the enamel attacking acids [9-10].

It is easy to show that when enamel is shaken *in vitro* with a fluoride solution (even as dilute as 1 mg L^{-1}), and subsequently washed it has a lower solubility than untreated enamel. However, the solubility of the enamel is reduced if the acid attacking it contains 1 mg L^{-1} of fluoride. Evidently, fluoride reduces the solubility of enamel, whether it is present in the enamel itself or not in the solvent. It is evident that this reduction in the solubility of enamels containing fluorides is due to the formation of fluoroapatite in the place of hydroxyapatite, since it is known that the former is less soluble than the latter. This is presumably due to the formation of a protective layer of calcium fluoride on the dissolving crystals of fluorapatite. An alternative theory is that apatite is formed only in the presence of fluoride; in its absence the more soluble crystals of brushite, $CaHPO_4$, or octa calcium phosphate, $Ca_8H_2(PO_4)_6.5H_2O$, are formed.

Since fluorides inhibit some enzymatic processes, the possibility must be considered that they could control caries by reducing the amount of acid produced by the bacterial in the saliva or in the layer of bacteria suspended in a protein matrix that deposits on teeth (known as "dental plaque") [9].

The fluoride in plaque is unlikely to come from the enamel. The incorporation of fluorides by the apatite of enamel is known to be a virtually irreversible process. The enamel could only be a source of fluorides for the plaque if the plaque dissolves the apatite of the enamel. But this could only occur to a very small extent, if at all, otherwise the fluorides of the enamel surface would decrease with age when in fact they increase. If the fluoride in the plaque is not derived from the enamel, it must come from the slow ticket of saliva, from the larger but intermittent washes with drinking water and other fluoride- bearing liquids or from food. Probably all these factors contribute to the cariostatic effect of fluorides, though which of them is predominant is not yet settled [9-11].

3.1.1.2. Fluorides in Bones

It is essential to know the function of fluoride ions in the structures, morphology, and physiology of bone since about 96 % of the fluoride in the body is deposited in hard tissues. The fluoride ion is unique in that it continues to be deposited in calcified structures after other bone constituents (calcium, phosphorus, magnesium, carbonate and citrate) have reached a steady state. Even if large amounts of these other constituents are administered, their concentrations, which reached their maximum early in life remain essentially unchanged. Fluoride in bone, on the other hand, increases very rapidly with higher fluorides levels in drinking water. However, age is an important factor in the extent to which fluoride is incorporated into the skeletal [8-10].

The current theory of bone formation postulates that collagen (the chief protein of the bone fibre) forms a matrix for a nucleation process in which calcium and phosphorus are deposited. This is followed by the formation of the mineral phase- called hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$.Thus, the collagen fibers act as a template for the deposition of the hydroxyapatite crystals. As fluoride ions are the same in size and shape as the hydroxy ions, they are able to replace hydroxyl ions, either partially or completely, in the apatite crystals; so that hydroxyapatite and fluoroapatite are able to co-exist in the mineral phase.

When fluoride is present, a definite improvement in crystal structure has been observed. Present methods can not definitely establish the position of an individual ion, but it is generally agreed that potassium, sodium, and citrate ions do not occupy positions in the lattices of biological apatite. Recent evidence suggests carbonate can replace the phosphate group, at least to some extent. When it does so, it is known to disturb the crystal structure. Although citrate is not incorporated into the lattice, it is believed to be adsorbed on the crystal surface, and it also disrupts the structure.

The beneficial effect of fluoride ions in these apatite crystals could be due to either or both of the following processes:

- a direct effect on the nucleation process causing larger crystals of hydroxyapatite to be formed;
- a displacement of such ions as carbonate and citrate, which are known to disturb crystallization.

More support is given to the second alternative by the observation that as the fluoride content of the bones increases, there is a corresponding decrease in carbonate and citrate.

3.1.1.3. Fluorides in the Treatment of Osteoporosis

Osteoporosis is defined as the loss of bone accelerated beyond the normal "physiological" rates. Most adults lose minerals from bone regularly through out their life. In women, this bone loss is enhanced for a year or two years after the menopause, so that bone mass may be ultimately less than half of that in young adults. In males, a corresponding acceleration appear at 60-65 years of age. Severe clinical manifestation of osteoporosis are: loss of cortical bone, which leads to fracture of long bones, and loss of trabecular bone, which may cause fractures in the spine. However, it was found that NaF has been used as a potential treatment for osteoporotic disease [2, 8-11].

3.1.1.4. Fluorides in Others

At high doses, fluoride can interfere with function of carbohydrates, lipid, protein, vitamin, enzyme, and mineralization.

3.1.2. Effects on Plants and Animals

The plants deficient in calcium and magnesium or aluminum are more vulnerable to effects of fluorides or that its effect depends on the availability of calcium in the plant. Michael *et al.* [2, 8-12] found plants grown in a nutrient solution deficient in calcium and magnesium and exposed to hydrogen fluoride had decreased top growth and increased foliar chlorosis and necrosis of the optical leaves. It was found that tomato plants fumigated with hydrogen fluoride showed less injury under conditions of high magnesium and calcium and enhanced injury under magnesium and calcium deficient conditions.

Moreover, fluoride reacts with and removes metals such as copper, iron, molybdenum, zinc, and magnesium thereby inhibits enzyme activity with special case forming MgF_2 with Mg. The major route of fluoride uptake by domestic animals is through ingestion. Chronic manifestations of excessive fluoride exposure are similar to those found in humans, i.e., severe dental fluorosis and lameness; this limits feeding and therefore impairs. Symptoms in livestock develop progressively at total dietary fluoride concentrations above 20-30 mg/kg dry matter [2, 8].

3.2. Toxic Effects of Fluoride

3.2.1. Toxic Effects of Fluoride on Man

The toxic effects of fluorides acute, resulting from a single massive dose, or chronic, resulting from large doses over a number of years. Many of the symptoms of acute fluoride intoxication are the result of its binding effects with calcium while that of chronic effect are the results of fluoride deposition in hard tissues [8].

3.2.1.1. Acute Toxic Effects

Acute fluorine poisoning is very rare but, in view of the wider use of fluorides in industry, agriculture, and the home, cases may more frequently in future. It usually results from the accidental ingestion of insecticides or rodenticide containing fluorides salts. Initial symptoms are secondary to the local action of fluoride on the mucosa of the gastro intestinal tract. Salivation, nausea, abdominal pain, vomiting and diarrhoea are frequent. Systematic symptoms are, however, diffuse abdominal pain, diarrhoea, vomiting accompanied by excessive salivation, thirst, perspiration and painful spasms of the limbs. Emergency treatment is to provoke vomiting and then to make the patient drink large volume of milk. Conventional treatment includes the intravenous administration of glucose in saline and gastric lavage with lime water to precipitate the fluoride [2, 8-11].

3.2.1.2. Chronic Toxic Effects

Chronic toxic effects from high exposure in man are primarily related to mottling of teeth and fluorosis, in which bone structure is affected. In man, the major manifestation of chronic ingestion of excessive amount of fluorides are osteosclerosis and mottled enamel.Chronic exposure to excessive fluorides causes increased osteoblastic activity [2, 9-11].

3.2.1.2.A. Chronic Effects on Dental (Mottled) Enamel

A pattern, known as dental fluorosis or mottled enamel, was described by Eager in 1901 among the emigrants from Italy.The term mottled enamel was first introduced by Black *et al*. [2, 8-14] who described the disease in detail. Although it occasionally affects primary teeth, dental fluorosis particularly affects permanent teeth.The severity of the mottling seems to bear a quantitative relationship to the fluoride level in drinking water, though regional climatic conditions may influence water consumption and hence the total fluoride ingest. Dental fluorosis occurs in man consuming water containing 1.5 mg L^{-1} or more of fluorides, particularly during the first 8 years of the life. Mottled enamel usually takes the shape of modification of tooth enamel to produce yellow or brown stains or an unnatural opaque chalky white appearance with occasional striations and pitting. The incidence and severity of mottling were found to increase with increasing concentration of fluoride in drinking water. Dean [12-14] categorized the extent of clinically observed mottling into 7 categories, ranging from “normal” to “ severe”. These are:

• Normal	the enamel is translucent, smooth, and presents a glossy appearance.
• Questionable	seen in areas of relatively high endemicity and occasional cases are border line and one would hesitate to classify them as apparently normal or very mild.
• Very mild	small, opaque, paper white areas are seen scattered irregularly over the labial and buccal tooth surfaces.
• Mild	the white opaque areas involve at least half of the tooth surface, and faint brown stains are sometimes apparent.
.• Moderate	generally all tooth surfaces are involved and minute pitting is often present on the labial and buccal surfaces (brown stains are frequently a disfiguring complication).
.• Moderately severe	pitting is marked, more frequent and generally observed on all tooth surfaces and brown stains if present, are of generally of greater intensity.
• Severe	the severe hypoplasia affect the form of tooth and stains are wide spread and vary in intensity from deep brown to black (this condition may sometimes be referred to as ‘ corrosion’ type of mottled `enamel).

In general, mottled enamel is the result of a partial failure of the enamel forming cells properly to elaborate and lay down enamel to the non-specific response to a variety of stimuli out of which is the ingestion of excessive amount of fluoride. Since mottled enamel is a developmental injury, the ingestion of fluoride following the eruption of the tooth has no effect. Mottling is; however, one of the first visible signs of an excessive intake of fluoride during childhood.

3.2.1.2.B. Chronic Effects on Bones

While dental fluorosis is recognizable, skeletal fluorosis does not become clinically stage. Early symptoms include pains in the small joints of hands and feet, in knee joints, and in the joints of the spine. In latter stages there is stiffening of the spine and limitation of movement, followed by curvature of the spine [2, 9-14].

In skeletal fluorosis, the bones are heavy and irregular and have a dull color.The sites of muscles and tendon insertions are abnormally prominent irregular bone may be seen along the attachment of muscles and tendons, there is thickening and calcification in most of the ligaments and in many capsular attachments and the thyroid cartilage is often calcified. Apart from this gross changes fluorotic bone increases in weight; the fluorotic skeletal may be more than twice as heavy as a normal skeletal of similar proportions. The chemical composition is also altered, with a marked increase of fluoride in the bone ash, lower carbonate, and citrate contents; the calcium and magnesium contents; however, remain normal.

Chronic exposure to excess fluoride also causes increased osteoblastic activity. Osteosclerosis is a phenomena wherein the density and calcification of bone are increased; in the case of fluoride intoxication, it is thought to represent the replacement of hydroxyapatite by the denser fluoroapatite. However, the mechanism of its development remains unknown. The degree of skeletal; involvement varies from changes that are barely detectable radiologically to marked thickening of the cortex of long bones. Numerous exostoses scattered throughout the skeleton and calcification of ligaments, tendons, and muscles attachment to bone. In its severest form it is a disabling disease and is designated as crippling fluorosis [2, 9].

3.2.1.2.C. Other Chronic Effects

Chronic effects on kidneys have also been observed, generally in persons with renal disorders. The effect of fluoride chronic on the thyroid glands are known as a result of high exposure. Fluoridated water has been blamed for a large number of chronic conditions ranging from constipation to brittle nails and from gonadal conditions causing "feminized males" to manic depression. It is also quite common for health officers to receive complains from local citizens about digestive disorders and other disabilities caused by fluoridated water-even before the fluoridation taken place [10-11].

across the solution boundary resulting in a potential difference between the two solutions. In making electrode measurements, it is important that this potential be the same when the reference electrode is in the standardizing solutions as well as in the same solution, otherwise, the change in the liquid junction potential will as an error in the measured specific ion electrode potential.

The most important variable which analysts have under their control is the composition of the liquid junction filling solution. The filling solution should be equitransferent. That is, the speed with which the positive and negative ions in the filling solution diffuse into the sample should be nearly as equal as possible. If the rate at positive and negative charge is carried into the sample solution is equal, then no junction potential can result [7].

4.2. Electrode Response

The electrode potential plotted against concentration on semilogarithm paper results in a straight line with a slope about 54-60 mV per decade. The time response of the electrode, i.e., the time required to reach 99% of the stable potential reading varies from several seconds in concentration solutions to several minutes near the limit of detection.

4.3. Linear Range

Several researchers [7] have proven that the electrode gave a Nernstian response in the fluoride ion concentration range from 0.1 to below 10^{-5} mol L^{-1}. The estimation of the lower limit is subjected to some uncertainties due to the variable liquid junction potential and the activity coefficient of the fluoride ion. The divergence from a linear relationship between the cell potential and log C_F is generally attributed to:

- solubility of the membrane;
- the presence of impurities in the supporting electrolyte;
- adsorption of the test ions on the walls of the container.

A detail study on the fluoride electrode has shown that the solubility of the membrane did not interfere with the proper functioning of the electrode where as the ions of the supporting electrolyte and the chloride impurities did. The two factors, namely solubility of the crystal membrane and adsorption of fluoride ions at the membrane solution interface, strongly affect the sensitivity of the LaF_3 electrode and thus determine the lower limit of detection of the fluoride electrode. It has been noticed by many researchers that the fluoride ion concentration in a saturated solution of LaF_3 can be measured from concentration solution up to approximately 10^{-7} mol L^{-1}. However, from the plots of E vs log a_F a value of 10^{-6} mol L^{-1} can be determined as the lower limit of detection. The fluoride membrane electrode responds in both neutral and moderately acidic media within the fluoride ion concentration range 1 to 10^{-5} mol L^{-1} or 10^{-6} mol L^{-1} [7].

4.4. Limits of Detection

In neutral solutions, fluoride concentration can be measured down to 10^{-6} mol L^{-1} (0.02 mg L^{-1}) fluoride. However, care must be taken in making determinations below 10^{-5} mol L^{-1} to avoid sample contamination. The upper limit of detection is a saturated fluoride solution [7] .

4.5. Reproducibility

Reproducibility is affected by factors such as temperature fluctuations, drift, and noise. With in the electrode's operating range (1 mol L^{-1} to 10^{-6} mol L^{-1}), reproducibility is independent of concentration; with calibration every hour, direct electrode measurements reproducible to ±2 % can be obtained.

4.6. pH Working Range

In a solution with a pH below 5, hydrogen ion complexes a portion of the fluoride ion, forming HF or HF^-_2, which can not be detected by the electrode. To free the complexed fluoride, the pH of solution must be adjusted to the weakly acidic to weakly basic region before making the determination. On the other hand, in basic solutions with a low fluoride content ($\leq 10^{-4}$ mol L^{-1} at a pH of 9.5 or above), the electrode responds to hydroxide and fluoride ion. The potential reading, caused by the concentration of both hydroxide and fluoride ion, is lower than it would be if fluoride alone were present. Hydroxide ion interferes with the electrode response to fluoride level when the level of hydroxide is greater than one-tenth of the level of fluoride ion present. For example, at pH 7, when the hydroxide concentration is 10^{-7} mol L^{-1} or less, there is no hydroxide interference with fluoride measurements. At pH 10, where the hydroxide concentration is 10^{-4} mol L^{-1}, there is no error at 10^{-2} mol L^{-1} fluoride. Addition of total ionic strength adjustor buffer (TISAB) to fluoride standards and samples avoid hydroxide interference or the formation of hydrogen complexes of fluoride. Therefore, the optimum working pH range for fluoride electrode is from 5-6 [7].

4.7. Interference

Cations and most anions do not interfere with the response of the fluoride electrode to fluoride. Anions commonly associated with fluoride, such as Cl^-, Br^-, I^-, $SO_4^{=}$, HCO_3^-, PO_4^{3-}, and acetate, do not interfere with electrode operation. The hydroxide ion is an electrode interference. However, some anions, such as carbonate or phosphate, make the sample more basic, increasing the hydroxide interference, but are not direct electrode interferences.

4.8. Temperature Effects

Since electrode potential are affected by changes in temperature samples and standards solutions should be within ±1°C of each other. At the 10^{-3} mol L^{-1} level, a 1°C difference in temperature results in a 2 % error. The absolute potential of the reference electrode changes slowly with temperature because of the solubility equilibria on which the electrode depends. The slope of the fluoride electrode also varies with temperature as indicated by the factor 'S' in the Nernst equation. If the temperature changes occur, pH meter and electrode should be recalibrated. The electrode can be used at temperature from 0-100°C provided that temperature equilibrium has occurred. For use at the temperatures substantially different from room temperature, equilibrium times of up to one hour are recommended. The electrode must be used only intermittely at solution temperatures above 80°C [7].

4.9. Determination of Fluoride with Fluoride Ion Selective Electrode

The purpose of the calibration curve is to enable the response of the electrodes in standard solutions to be compared with the responses in samples. In order for the comparison to be valid, both standards and samples must be treated identically. Thus, any reagent added to samples before measurement should also be added to standards in the same proportions, so that the background compositions of samples and standards are identical.

The calibration curve is prepared by making a series of solution spanning the anticipated range concentrations of the determinand in the samples. The ISE and reference electrode are then immersed in the pretreated and continuously stirred standards in ascending order of concentration [7]. The potential of the cell is measured in each solution and the resultant potential are plotted against the logarithm of the determinand concentration to produce a calibration graph or the concentration of the determinand (fluoride) in the sample can be calculated by the formula derived from the Nernst equation given below

$$E_s - E_x = \Delta E = S \log C_x/C_s$$

which can be rearranged to : $C_x = C_s \times 10^{\Delta E/S}$ (3)

In standard addition method alternatively called 'the known addition method' the ion selective electrode and reference electrode are immersed in the sample and the equilibrium cell potential is recorded; a known volume of the standard solution of the determinand is then added and the new equilibrium cell potential, and hence, the change in potential, is determined. The initial concentration of the deteminand in the sample may be calculated from the equation:

$$C_x = C_s V_s [(V_x + V_s)] 10^{\Delta E/S}]^{-1} \qquad (4)$$

5. DEFLUORIDATION METHODS

Fluoride is considered as an essential element for prevention of dental caries and is added to many toothpastes and some water supplies for promotion of dental health. However, in high concentrations, dental fluorosis (mottled enamel), and/or skeletal fluorosis can result. The effects of both diseases are incurable through medical treatment. Therefore, defluoridation is the simplest method of reducing excess fluoride. The World Health Organization has set an optimum value of 1.5 mg L^{-1} for F^1 in drinking water as a result of its potential detrimental to health effects.

Several methods have been suggested from time to time for removing excessive fluorides. These methods may be divided into two basic categories: those based upon the additions of chemicals to water which form precipitates or co-precipitates; and those based upon an ion-exchange process or adsorption during treatment. The chemical treatment methods include the use of lime either alone or with magnesium salts, and aluminum salts either alone or in combination with a coagulant aid. The materials reported to have been used in adsorption process include, magnesia, activated alumina, activated carbons, and those of ion-exchanger include processed bone, natural or synthetic tricalciumphosphate, hydroxyapatite, animal bone, fish bone, florex, zeolite, etc.

Other methods include the addition of materials like magnesia, calcium phosphate, bentonite, fuller's earth, and diatomaceous earth, to fluoridated water mixing and their separation from water by setting and/or filtration [2, 12-14].

5.1. Precipitation Methods

5.1.1. Aluminum Sulphate

Good mixing and good flocculation have been found necessary for the maximum removal of fluorides with aluminum sulphate. Chlorides and sulphates concentrations as high as 1000 mg L^{-1} has no effect on the removal of fluorides by aluminum sulphate.The optimum pH range for the removal of fluorides with aluminum sulphate lies between 6-7.5 with some slight advantage at a pH of 6-7 [14, 20, 25]. The result obtained shows that the percentage of the fluoride removal gradually decreases with increasing pH.This decreasing trend with pH is expected because of the following competing complexation and interference from such as aluminum, magnesium, iron, calcium, and anions of sulphate, bicarbonate, hydroxyl, etc.

$$AlF_3 + 3\,OH^- \rightleftarrows Al(OH)_3 + 3F^-$$

The overall pH study; however, shows that defluoridation by aluminum sulphate is still efficient (more than 79 %) at pH values that encompass the pH of water (pH 5-7.5) normally required for drinking.

5.1.2. Aluminum Hydroxide

The fluoride removal efficiency of aluminum hydroxide was found to be 10.8 mg F^- per g of aluminum hydroxide [13, 20, 34]. Precipitates as hydrates $Al(OH)_3$ will occur with increasing pH since the $[OH^-]$ increases.The precipitation of $Al(OH)_3$ commences at about pH = 4, and is completed when the pH lie between 6.5-7.5. Hence, fluoride added to water competes with the following equilibrium to precipitate as aluminum fluoride whose reaction is:

$$Al(H_2O)_6^{3+} + 3F^- \rightleftharpoons AlF_3 + 6H_2O$$

5.1.3. Lime

Lime is the cheapest chemical employed for the removal of fluoride from wastewater. However, it is impossible to reduce the fluoride level to 1 mg L^{-1} using only lime. The solubility of the precipitate formed, CaF_2, is about 7.7 mg L^{-1} as fluoride. Skripatch *et al.* [12-14]. Proposed a scheme for fluoride removal using lime whereby large amounts of fluoride were removed by reaction with superphosphate and calcium hydroxide or aluminum sulfide for the removal of the residual fluoride. The drawbacks of precipitation method include the necessity for the additional reagents, higher shipment and treatment costs, and the large volume of sludge produced. Filter alum (aluminum sulphate) in some cases is not economically feasible because of high dosage requirements.

5.1.4. Magnesia

Crystalline magnesium hydroxide was obtained by reacting a magnesium salt with milk of lime. The precipitate was filtered, washed, and dried.The dried products was calcined at 1000°C for 3 h to obtain magnesia. A study using magnesia revealed that a dose of 1500 mg L^{-1} magnesia and a contact period of 3 h was required to reduce the fluoride content in the water to recommended value, 1 mg L^{-1}, and the study also revealed that magnesia removed the excess fluorides, but large dose were necessary. Furthermore, the pH of treated water was beyond 10 and its correction by acidification and recarbonation is necessary. All these added to the cost and complexity of the operation. The study concluded using 95 % magnesia thus may give the limitations of this medium at implementation level. Among the contributing factors are the high initial cost, large concentration required, alkaline pH of the treated water and complexity of the preparation of magnesia are the inhibitive factors to render its acceptable in the field [12-14].

5.1.5. Alum and Lime

Nelgonda technique [12, 20 ,25], that requires the additions of alum and lime, was developed in India since 1800s. It has been used in domestic as well as community level in India. The limitations of this method are: the daily addition of chemical, large size of sludge production, ineffective with water sources having high total dissolved salt, and defluoridated water should be checked to ensure that there is no aluminum content arising from the alum. In addition, the technique is found to be ineffective in removing fluoride from drinking water because in the defluoridation process fluoride was converted into a solution of aluminum complex and only 18-33 % removed in the form of precipitate. The hitherto positive assessment of the method results from an analytical error.

5.1.6. Sodium Aluminate ($Na_2Al_2O_4$)

Sodium aluminate affected the removal of fluorides when using as a coagulant. A dosage of 24 and 41 mg L^{-1} of sodium aluminate reduced the fluoride content of 5.0 mg^{-}L of test solution to 4.8 and 4.4 mg L^{-1}, respectively. Hence, the defluoridation capacity of the medium was found to be 25%. It was found to be the least defluoridating agent in comparison to the other media. This is presumably due to the ion effect soluble NaF which might be formed in the solution as a result of the interaction between sodium aluminate and fluoride standard [13-14, 20, 25].

5.1.7. Silica Gel, Sodium Silicate and Ferric Salt

A contact filter containing 500 mg L^{-1} of silica gel reduced the 6 L of a 5 mg^{-1}L F solution to 1 mg L^{-1} at filter rate of 350 mL/min. Treatment of silica gel with water gave high magnitude of efficiency.

Treatment of waters with sodium silicates (250 mg L^{-1}) and aluminum sulphate or sodium aluminate gave less magnitude of efficiency than given by the same treatment without the sodium silicate.

It is well known that ferric chloride complex is only slightly ionized. Therefore, there was a chance that fluorides might removed by this coagulant. The defluoridation capacity of ferric chloride was found to be 55 % [20, 25].

5.1.8. Magadi

Purification of fluoride contaminated water using Magadi (Trona) was found to be efficient. Magadi (Trona) was found to be workable both in batch and column modes as a defluoridating agent. The fluoride removal capacities observed for Magadi was 70 % for batch experiment and 75 % for column one. In using Magadi as a defluoridaing agent 10 mg L^{-1} water could brought down to the WHO recommended limit (1 mg L^{-1}) [19]·

5.2. Adsorption Method

5.2.1. Activated Alumina

The activated alumina was found to remove the fluoride concentration of 2-8 mg L^{-1} from underground waters through adsorption. The rate of fluoride adsorption on smaller sized particles was significantly greater than larger sized particles. The optimum pH for the fluoride removal by alumina was found to be 6. However, it could be advisable to remove fluoride at pH 4 to 5 where less competition from silicate is experienced. Silicate and phosphate from 5-80 mg L^{-1} were found to have very little effect on fluoride removal efficiency. Sulphate in the concentration range from 100-1600 mg L^{-1} were also found to have very little effect on fluoride removal efficiency. It was suggested that the single most important factor affecting fluoride removal efficiency was the hydroxide and bicarbonate alkalinity of the water. The removal capacity of the medium was found to be about 800 mg F^- per kg of alumina [2, 12-14, 20].

5.2.2. Activated Bauxite

The basic principles of fluoride removal using activated bauxite are adsorption of fluoride on activated surfaces and then regeneration of an expanded medium to remove all fluoride ions from bauxite-fluoride complex before return to the treatment.

Activated bauxite removes fluorides species from water due to hydrolytic adsorption. It will remove anions below pH 9 and cations above it. The affinity of bauxite for an anion seems to be inversely related to the solubility of its aluminum compound. Therefore, when treated with an acid solution, bauxite behaves like anion exchanger and fluoride is very selective [12-14, 20, 25].

5.2.3. Activated Carbons

Most of the carbones prepared from different carbonaceous sources showed fluoride removal capacity after alum impregnation. Activated carbones removed about 320 mg of F^- per kg of carbons and showed a maximum removal efficiency at pH 7. The activated carbons was regenerated by soaking the spent material in 2 % alum solution for 24 hours. Activated carbones prepared from cotton waste, coffee waste, coconut waste, etc., were used for defluoridation but found to be limited to laboratory only [13-14].

5.3. Ion-exchange Methods

5.3.1. Activated Animal Bone

Raw cattle bones were heat activated in a simple low cost kiln at a temperature below 600°C which doesn't destroy the apatite. The bones were crushed and used as filter materials in columns for defluoridating water required for drinking. Laboratory analysis gave F^- removal capacity of 3.8 mg F^- per g heat treated bone with a residual fluoride concentrationof 7.88 mg L^{-1} using a filter column for 10 mg L^{-1} initial fluoride concentration.

The use of bone char media in fluoride removal in water was known over forty years ago. The fluoride removal capacity of the materials was reduced during each successive regeneration. This factor discouraged further development on the use of bone charcoal. Furthermore, because of the problems related to the bad taste of the treated water, cost and availability of the raw material, bone char fluoride removal failed to gain wide acceptance and hence has been confined to the experimental material. Recently, the use of bone char has reappeared with WHO recommended it to be used in developing countries where drinking water contains excessive fluorides [13-14, 22].

5.3.2. Fish Bone

Fish bone is comparatively cheaper material sources in fish cultivation areas. Fish bone charcoal was prepared by carbonizing the cleaned and pulverized fish bone in an electric furnace in a closed retort at 100°C for 2 h. The cooled material was then sieved to get the required size having geometrical mean diameter of 0.549 mm. The material was thoroughly washed with distilled water, oven dried at 103°C, desiccated, and stored in air-tight containers.

In a continuous flow, fixed bed column operation, the efficiency and system cost depend on the removal capacity of the media, i.e., the amount of solute adsorbed per g of the adsorbent. This capacity is a function of several factors such as flow rate, column bed depth, initial solute concentration, pH, temperature, and desired quality of the treated water [23].

5.3.3. Processed Bone

Bones are allowed to degreased, dried, and pulverized to get the required size. The powder is carbonized in a closed retort at about 750-950°C. The product was found to have tricalcium phosphate and has a capacity to remove 1500 mg L^{-1} of F per kg of medium. After saturation with fluorides, it can be calcined at around 400°C under restricted air supply to restore the adsorbing capacity of the char. Alternatively the bed may be regenerated by NaOH [13-14, 22].

5.3.4. Bricks and Cement

Freshly burnt bricks are freely available in dental and skeletal fluorosis endemic areas. In addition to its low cost in replacing the filter medium, it renders easy operation at domestic level, negligible maintenance cost and the absence of environmental hazards in releasing the used filter medium are the other important features in the new units. The trained beneficiaries had the capacity to change the filter medium in time in order to get best output from the defluoridators. The efficiency level of these defuoridators change from 85 % removal at the start and tapers down to 25 % removal at the end of the cycle. These defluoridators have the capacity to reduce the fluoride content from 5 mg L^{-1} to 1 mg L^{-1} which conform to WHO standards for fluoride removal in drinking water. These defluoridators have got social acceptance and technical feasibility at domestic level in different parts of the world [13-14, 57].

The burnt bricks and cements have silicates, aluminates, and hematite. When this is soaked in water for several hours, these oxides get converted into oxyhydroxides of iron, aluminum, and silica. The Si-O and Al-O bonds are much stronger than Fe-O bonds. The geochemistry of fluoride ion (ionic radius 1.36 Å) is similar to that of hydroxyl ion (ionic radius 1.4 Å) and these can be exchanged easily between them. As it takes a minimum of 4 h for the ion exchange to take place, it is advocated to draw the water in the morning and evening. The upward flow technique used, prevented the sand particles mixing with water.

5.3.5. Florex

Florex is a trade name for a mixture of tricalcium phosphate and hydroxy-apatite. It reduces 10 mg L^{-1} of standard fluoride solution to 2.5 mg L-1. The fluoride removal capacity of the medium is 600 mg of F^- per liter and is regenerated with 1.5 % NaOH solution. Florex was implemented in pilot plants in different sites in U.S.A. but obtained without much success owing to high attritional losses, and the plants were abandoned [12-14].

5.3.6. Zeolite

It is apparent that fresh synthetic zeolite is capable of removing fluorides from waters but that the capacity is smaller than anticipated. The facts that small removals were noted for short periods following regeneration with salt or NaOH can be explained on the bases of preferential adsorption [12-14, 20, 25, 34-36].

5.3.7. SyntheticTricalcium Phosphate

Synthetic tricalcium phosphate is prepared by reacting phosphoric acid with lime. It has a capacity to remove 700 mg of F^- per litre. The medium is regenerated with 1 % NaOH solution, followed by a mild acid rinse [13-14, 20].

5.3.8. Ion-exchange Resins

Strong base exchange resins remove fluorides either on hydroxyl cycle or chloride cycle along with anions. Since the proportional quantity of fluoride as compared to other anions is very small, the effective capacity of such resins works out quite low. There are no known commercial anion exchange resins which are selective for fluoride only. Some inorganic ion exchanger may include complex metal chloride, silicate, formed from barium or ferric chloride with silicic acid, also exchange fluoride for chloride [13-14, 25].

Polystyrene anion exchange resins in general and strongly basic quaternary ammonium type resins in particular are known to remove fluorides from water along with other anions. Bhakuni [17-18] had studied on the following resins on bench scale: polyanion exchange resin (NCL), Tulson A-27, Deacedite, FF-1P, Lewatite, MIH-59, asndAmberlite, IRA-400.

Cation exchange resins impregnable with alum solution have been found to act as defluoridating agents. Many workers have been used cation exchange resins after treatment with alum solution for defluoridation. Venkataraman, *et al.*[12, 29] reported that cation exchange resins work effectively in removing fluoride from water.

Carbion is a cation exchange resins of good durability and can be used both on sodium and hydrogen cycles. It has a bulky density of 680 g L^{-1} and indicated to have an average fluoride removal capacity of 320 mg F^- per litre of carbion.

5.3.9. Defluoron-1

Defluoron-1, a sulphonated saw-dust, impregnated with 2 % alum solution was developed by Bhakuni [17-18] in India. It was prepared by treating required size of saw-dust with sulphuric acid, washing the excess acid by soaking sulphonated product in alum solution for 24 h and finally washing to remove the excess alum. The recovery of sulphonated saw-dust product was found to be 56.3-69.3 % of dried saw dust. The bulk density of this medium is 620 g L^{-1} .

The average fluoride removal capacity of sulphonated saw-dust was found to be 600 mg L^{-1} F^{-} per kg of medium. The medium was tested to have poor hydraulic properties and suffered from heavy attritional losses [12-14].

5.3.10. Defluoron-2

Defluoron-2 is a also a sulphonated coal and works on the aluminum cycles. To over come the problems with saw-dust carbon, and defluoron-1, a medium called 'defluoron-2' was developed for the removal of fluorides from drinking water. Extensive trials with the medium have shown that, it doesn't suffer from most of the handicaps like some of the indigenous materials. It was found to give the best results with one bed volume of 4 % (w/v) alum solution as regenerants. The life of the medium was found to be 2-4 years. The average fluoride removal capacity of the medium was about 500 mg F^{-} per litre of the test solution [13-14].

5.4. Other Defluoridation Methods

5.4.1. Fluoride Removal by Plants

In an attempt to find out an alternative media for defluoridating agent using plants product was investigated.The seeds, roots, and leaves of drumstick plant (*Moringa species*) and alkali extracted mycelial biomass (biosorbent) was found to be effective in sequesing fluoride from fluoride containing waters. When kept overnight, the fungal biosorbent removed fluoride to an extent of about 50 %.The kinetics of fluoride removal exhibited a rapid phase of binding for a period of 1 h and a slower phase of binding during the subsequent period.The extent of defluoridation of mycelial biomass was dependent on the initial pH of fluoride containing water and decreased with increasing pH [15].

Attempt to harness microbial biomass for the purification of polluted water from industrial sectors appeared promising. Live and inactivated fungal biomass exhibit interesting metal binding properties due to the presence of functional groups like amino acids, amide, carboxyl, hydroxyl, sulfhydryl, etc. in the cell walls. The biosorption involves direct exchange of toxic heavy metal ions with the resident Ca^{++}/Mg^{++} ions of the biosorbent. Fluoride binding by the fungal biosorbents appear possible considering their Ca^{++}/Mg^{++} content and the known affinity of Ca^{++} and Mg^{++} for fluorides ions [16].

The use of biosorbents (bacterial, algae, and fungal) as a defluoridating agent for scavenging heavy metal cations from polluted waters was tested. In mean time the use of these media for removal of hazardous anions like fluoride, nitrates were also investigated.The results revealed clearly demonstrate the ability of alkali treated mycelial biosorbent can be used to bind fluoride (biodefluoridation).The biodefluoridation is rapid and diminishes with repeated use. Mass dependence and pH influence further substantiate the authenticity of the observed biodefluoridation by the biosorbent. Lower binding at higher pH could be due to competition between fluoride and hydroxyl ions for fluoride binding sites. The mechanism of fluoride binding by the biosorbent is not clear.The organic matrix of the biosorbent contained calcium and magnesium ions. It is possible that the calcium and magnesium ions are responsible for binding fluoride.The primary amino groups could also get protonated at acidic pH and bind fluoride [15].

Traditionally in our country plant seeds and leaves have been used for water treatment and purification, especially in rural areas. These plants are *Moringa families* whose seeds and leaves or stems, and roots have widely used to reduce turbidity of drinking water.The seeds of *Moringa oleifera* were best coagulants as well as clarifying agents whose efficacy was similar to alum. Further it was found to soften hard water by precipitation, independent of the pH. The seeds are considered to be a good source for calcium and magnesium suggesting a possibility of its capacity to absorb fluoride during the treatment. Moreover, its physico-chemical analysis revealed that the seeds contain as much as 20 % of the oil which could play a role in the clarification. A concentration of 200 mg L^{-1} of *Moringa oleifera* reduced the turbidity by 98 %; this value of efficiency is more than alum (aluminum sulphate and alumina), used in modern water treatment

To clarify 40 L of water, about 30 crushed seeds are required. One mature tree produces about 5500 seeds per year, which is sufficient for about 7000 L of water. In Ethiopia *Moringa oleifera* is routinely found in south and east parts of the country [16].

Maerua subcordata, a much branched shrub was also adopted for treatment and purification of water by the tribes living in lower Omo River in South Nations and Nationalities Peoples' region [15]. In this plant , the root is sliced and stirred in muddy water. After 30 min 1 L of saturated muddy water was almost become clear. *Maerua subcordata,* is most likely contains an ingredient of a quaternary ammonium compound which can cause intoxication in high concentrations.

Similarly *Moringa stenopetala* (tree cabbage) can be even more effective [15-16]. The study conducted on *Moringa stenopetala* revealed that its seeds contain by far the most efficient plant-produced clarifying agent in the world, acting with a dose at least 8 times lower than that of alum. No toxic ingredients have been found, the taste of the water is improved and there is no effect on pH, alkalinity, or conductivity.

5.4.2. Saw Dust Carbon

Bhankuni [17-18] prepared a carbon from saw dust obtained from saw mills processing woods like sagon, sheesham and teak the material by heating in a closed vessel and allowing the tume to escape. The carbonized saw dust, quenched in a 2 % alum solution, was washed free of excess alum. On exhaustion, the carbon was regenerated by passing through bed volumes of 0.5 % alum solution. The defluoridating capacity of the carbon was reported to have been reduced progressively during the first 18 cycles to remain constant at about 160 mg F^- per litre of medium. The material had the problem of excessive attritional losses and appreciable head loss [12-14].

5.4.3. Serpentine

Serpentine is a mineral name which applies to the material containing one or both of the minerals, chrysotile and antigorite.The composition of the mineral closely corresponds to the formula $Mg_6Si_4O_{10}(OH)$. The material is green or yellow and is available in some parts of the world. To test the removal capacity of serpentine from waters, the green and yellow varieties were studied for their defluoridation capacity.The maximum defluoridation capacity of serpentine was found to be 60 %. The serpentine is not regenerable and requires to be filled each time after treating with the test solution. It was concluded that cost of defluoridation is prohibitive with serpentine [12-14].

6. AIM AND SCOPE OF PRESENT INVESTIGATION

The foregoing reviews reveal that fluoride is one of the chief inorganic anions of the body which is largely used during the child growth period when it is incorporated into hydroxy-phosphate of the enamel; to modify it in a way that makes it stronger and more resistant to decay and acids. If a trace of fluoride is present either in toothpaste, by the artificial fluoridation of drinking water, or by the application of the dentist of fluoride dressing, some of the hydroxylapatite in the enamel is converted to fluoroapatite which is more resistant to acids and decay. The fluoroapatite fits better into the crystal than the hydroxide ion and this makes the enamel tougher and more acid resistant [12-14, 31-34].

Deficiency of fluoride causes tooth decay known as dental caries. When fluoride is consumed in proper quantities it helps in the prevention of dental caries and strengthening of teeth and bones. Dental caries result from the action of bacteria on teeth. The most common of which is strcptocus mutant. The first even in the development of caries is the deposit of plaque, a film of precipitated products of saliva and food on teeth. A larger of bacteria inhibit this plaque and are readily available to cause caries. When carbohydrates are available the metabolic systems of bacteria are strongly activated and also multiplied. In addition they form acids particularly lactic acid. The lactic acids are the major out put in the formation of caries because the calcium salts of the teeth are slowly dissolved in a highly acidic medium.

Low level of fluoride are required for animals including humans and have beneficial effects on teeth and bone structures. Taking health effects into consideration, World Health Organization, WHO, has set an optimum value of 1.5 mg/L as the maximum permissible limit for fluoride in potable water.

In contrast to the cause of dental caries, a prolonged exposure to high level of fluoride in drinking water causes dental and skeletal fluorosis-chronic fluoride poisoning [31-35]. Surface water seldom contain fluoride beyond 1.5 mg/L, where as excessive fluoride may be present in ground waters depending on the presence of fluoride rich minerals as well as hydrogeological conditions. The actual amount of fluoride in the optimal range is dependent on the average ambient temperature of the atmosphere.

Dental fluorosis is thought to occur due to high fluoride intake in children before the eruption of the permanent teeth, usually from birth to 12 years. Dental fluorosis changes the structure and appearance of tooth enamel. At low fluoride concentration, tiny striations are formed. Higher concentration causes irregular brown patches and at even higher concentrations the enamel becomes brittle and may chip easily. These changes occur during the year of tooth calcification, age 1-12 years [32-36].

The other health problem that is brought by the extremely high accumulation of fluoride in the bones is skeletal fluorosis [8-14, 33-36] . Skeletal fluorosis occurs due to consumption of high amount of fluoride over 10 mg/L for a long period of time. In the most extreme cases fluoride accumulation in bones result in spinal cord compression. The bones of victims of skeletal fluorosis become rigid and brittle and consequently they are more liable to fracture.

Skeletal abnormalities caused by excessive fluoride range from increased bone density to crippling fluorosis. Early harmful effects of fluoride, usually in the young adults, are vague pains in the joints of hands, feet, knees and spines. As the person gets older, movement of the joints is limited and spine becomes stiff. Other possible effects of long term fluoride consumption include kidney problems, and an increase in the function of parathyroid gland which regulates calcium metabolism. However, the amount of fluoride in drinking water which causes harmful effect on humans varies in different part of the world. A person's age, nutritional state, economic status, diet, and individual variations in fluoride absorption and intake, as well as climate and drinking water composition affect the result of a given fluoride concentration [13-14, 31-34].

Both dental and skeletal fluorosis are prevalent in the Rift Valley Regions of Ethiopia because of high fluoride water that originates from ground waters (springs and boreholes). Endemic fluorosis-chronic fluoride poisoning is widespread in the East Africa Rift System, including the Ethiopian Rift Valley Regions, where it is associated with highly fluoridated drinking water in areas of acidic volcanic rocks. Fluoride levels in the Ethiopian Rift Valley Regions are generally higher in the ground water than in surface water, posing a health risk to the communities depending on wells for their drinking water. Fluoride concentrations between 1 mg/L and 36 mg/L have reported from the areas of endemic dental and skeletal fluorosis in the Ethiopian Rift Valley Regions. Accelerated population movements in to the Ethiopian Rift Valley Regions as part of resettlement programs, commercial agriculture and industrial development, and rapid urbanization require comprehensive assessment of the public risk posed by fluoride and of appropriate and feasible control measures. A limit of 0.7 mg/L has been recommended for hot climates, where water consumption by humans is highest [8-14, 31-36].

The effects of fluoride in drinking water on animals are analogous to those on human beings. Studies in Australia found the development of exostoses of the long bone and mandibles in mature sheep, as well as the abnormal development and ear of teeth erupted by young sheep exposed to excessive fluoride [20, 25].

Development of fluoride treatment began immediately following the discovery of fluoride as a cause of dental fluorosis in the late 1920s. Since then many methods and materials have been studied for fluoride removal. In general there are two methods for the removal of fluoride from water.

Precipitation methods involve the additions of chemicals and the formation of fluoride precipitates or coprecipitates. The chemicals adopted include: lime [13], magnesium compounds such as dolomite [20], calcium chloride [25], and aluminum sulphate [13-14, 20]. It has been used in domestic as well as community levels in India. Limitations of these methods are: the daily addition of chemicals, large volume of sludge production, and not effective with water sources having high total dissolved solid and hardness [13-14, 25].

The adsorption methods involve the removal of fluoride by ion exchanger or by chemical reaction with an adsorbent. In the adsorption methods, samples containing fluoride is retained on the adsorbent due to physical, chemical, or ion-exchange interactions. Ion-exchange include: zeolite [12-14], hydroxylapatite [31-36], and superphosphate [13-14, 31-35]. Adsorption by activated alumina [2, 13-14, 31-45], activated bauxite [20, 25], activated carbons [13-14] and clays [34, 43] are the usual means of defluoridation. The various materials for the defluoridation are: processed bone (peculiarly bone meal and bone char) [12, 22], natural and synthetic tricalcium phosphate [13-14, 34-36], magnesia [12-14], magnesium carbonate (dolomite) [20, 34], hydroxylapatite [13, 34], activated alumina [2, 13-14, 36], activated bauxite [25,34], activated carbons [12-14], alum [13-14, 20, 25], sulphonated coals [12-14], serpentine, iron Chloride [12-14], lime [12-14, 20], bentonite, fuller's earth, and diatomaceous earth [13-14]. All these materials suffer from one or more of the drawbacks of high initial cost, lack of selectivity for fluorides, poor fluoride removal capacity, separation problems, complicated and expensive regeneration.

Hence, most of the available materials and techniques for defluoridation are expensive and are not technically feasible for removing fluoride from the ground water supplies in the Ethiopian Rift Valley Regions. Thus, the need to find and investigate locally available defluoridating media for safe and easy utilization at both community and household levels is of great importance.

A recent report from our laboratory indicated that activated alumina is efficient for removing fluorides from ground waters in the Ethiopian Rift Valley Regions. Kaolin was also found to be efficient although not regenerated and accessible [2, 43], however, diatomaceous earth was found to be inefficient [2].

By the use of modern technology excessive fluoride may easily be removed from water. High technical methods, however, are rarely applicable and accessible under rural, third world conditions. Hence, water treatment for removal of fluorides is not generally simple and inexpensive. The availability of inexpensive, accessible and effective media for the removal of excessive fluorides in the Ethiopian Rift Valley ground waters at community and household would undoubtedly be a boon to the public health investigators. The capacity of the various defluoridation, problems in operation, the cost of defluoridation and limitations in their applications will be taken in to consideration for study of media for removal of drinking waters in the Ethiopian Rift Valley Regions.

Thus, simple techniques for low level defluoridation of drinking water in the Ethiopian Rift Valley Regions ground waters at community and household levels, are needed in order to remove fluorides related health cases in the growing child.

Clays are reported to be an efficient fluoride remover from natural waters [34]. Preliminary studies in our laboratory have shown that clay pots is a good medium for absorbing high fluoride concentration from waters [34, 43]. The advantage of clays pot is that it can be regenerated and reused after being adopted, as well as clays are accessible and inexpensive. Furthermore, clay pots have traditionally been used for storage of drinking water in the Ethiopia. The clay pots are most often made from locally available clay or soil, and are thus readily available.

However, no systematic investigation has been made on clays as to its defluoridating capacity on Ethiopian Rift Valley ground waters. Therefore, it is necessary to study the fluoride binding capacity of the clays, and thus, it is worthwhile to extend the study to the types of soils (clay, laterite), the origin of the soil (relative altitude), variable volumes, variable time of contact, as well as the pH level of the water from the ground waters of the Rift Valley Regions of Ethiopia.

This project is concerned with an investigation of defluoridation of ground waters using indigenous clays. The objectives of the present investigation are:

6.1. OBJECTIVES

- To investigate the fluoride binding capacity of clays from different regions of Ethiopia with the Ethiopian Rift Valley ground waters.

- To assess the effect of altitudes of clays on the defluoridation efficiency.
- To study the time of contact of ground water samples with clays.
- To study the effect of volume of water samples on defluoridation efficiency of clays.
- To study the effect of stirring of samples with clays.

7. CLAY

7.1. Definition of clay Nature

The clay fraction probably is the most important components of surface deposits and soils, whether in terms of origin, agricultural or engineering use, or as a factor in the environmental processes-physical, chemical, and biological. The term 'clay' may refer to very fine particles, regardless of their mineralogy or may refer to a definite series of minerals. The word clay is the secondary minerals, together with organic matter, constitutes the active fraction of the soils with respect to most chemical and physical properties with particle size range below 2 μ (0.02 mm). Fine and colloidal clay is considered to be made up of particles with an effective diameter below 0.2 μ (0.02 mm) and definitely possessing colloidal properties. Clay is cohesive, it holds soil aggregates together and controls many soil structures. Clay retains moisture, and thereby impede the movement of the water and air in the ground. They also hold plant nutrient, some in the form of available for plant use, others in unavailable forms. The plasticity of the clay is partly a function of the particular clay mineral [26-28].

A clay soil consists of clay and non-clay particles, where the clay is any soil with particles of 2 μ (0.02 mm) and less and hence the clay minerals are in amount high enough to influence the physical properties of the soil. Because of their small size, some clay particles present a relatively large specific surface for adsorption. Negative charges developed at clay and organic matter surfaces are able to adsorb cations, which may under go stoichiometric exchange with mobile cations in soil.

7.2. Size and Shape of Clay Particles

Although there is no sharp boundary between particle size of clay and non-clay, it has been shown that there is a general tendency for the clay minerals to concentrate in a size range smaller than 2 μ and larger clay particles breakdown easily to this size slaked in water.

On the other hand, non-clay minerals usually are not present in particles much smaller than 1 to 2 μ. However, most of the so called clay soils contain non-clay as well as clay minerals. Therefore, the best split of the two clays obtained at the size of 2 μ.

Most particles larger than about 5 μ can be represented as sphere like or cube like particles with reasonable accuracy. On the other hand, most particles smaller than 5 μ are shaped like a plate, the length or the width of which is 5 to 300 times its thickness. The plate shape, which most particles possess, is well illustrated by the electron photomicrography of a kaolinite clay particles with an equivalent area diameter of 1.3 μ and thickness of 0.083 μ.

7.3. The Basic Clay Mineral Structure

Clay minerals are mostly secondary hydrous aluminum silicates which comprise the bulk of the clay fraction of soil, and composed of two sheet structure, where one containing silicon atoms and the other containing aluminum atoms.

Many sophisticated instruments and methods have been used to study the crystalline structure of clay minerals. These methods are X-ray diffraction, IR, petrographic, electron and ultramicroscope and differential thermal analysis among others.

Clays are layer of lattice minerals, resulting from different stacking arrangement of the two basic building blocks. These two blocks are described by Grim [26] as follows:

- One is an octahedral unit in which an aluminum, iron, or magnesium atom is enclosed in 6 hydroxyl or oxygen atoms having the configuration of an octahedron. The octahedra units are put together into a sheet structure, which may be viewed as two layers of densely packed hydroxyls, with the cation between the sheet in the octahedral co-ordination. The octahedra lie on their sides and are oriented with their long axes parallel. The oxygens and hydroxyls atoms are in planes, one below and the other above the plane of aluminum atoms, and these oxygens and hydroxyls form a hexagonal network. The hydroxyls (OH^-) substitute for oxygens (O^{2-}) in the basal plane and share oxygens with the apices of the tetrahedra of the silica sheet, the charge thus become balanced and the two sheets are tightly joined.

- The second building block is a silica tetrahedral unit, in which four oxygens or hydroxyls having the configuration a tetrahedron enclose a silicon atom. The tetrahedra are combined in a sheet structure so that the oxygens of the bases of all the tetrahedra are in a common plane, and each oxygen belongs to two tetrahedra. The pyramids, or tetrahedra, are arranged in an orderly pattern, with their apices all pointing in the same direction and the bases joined at the corners in 6's to form a hexagonal network of pyramids. In this structure, the oxygens atom in basal plane are shared by the hydroxyls (OH^-) substituted for the oxygens, O^{2-} . There remains in the structure an excess negative charge, and this is what joins the silica to the positively charged alumina sheet. The silica tetrahedral sheet alone may be viewed as a layer of silicon atom between a layer of oxygens and a layer of hydroxyls.

The thickness of the octahedral layer is 5.05 Å whereas that of the tetrahedral layer has a thickness of 4.93 Å.

The clay minerals are classified into different categories, namely, kaolinite, montmorrillonite, illite (hydrous mica), glauconite (a mica like clay), chlorite and others. Sheets of silica tetrahedra and alumina octahedra are the fundamental structural units of the more important clay minerals.

7.3.1. Kaolinite Clay Mineral

It is the simplest and most stable of the clay mineral structures.The kaolinite clays include at least 5 mineral members, four of which have the same composition of $Al_4Si_4O_{10}(OH)_8$. They are kaolinite, nacrite, dickite, and hallosysite. It is referred to as 1:1 layering. Because their structures consist of a silica sheet and a gibbisite (alumina) sheet joined through common oxygens ions. The silica and alumina sheets form stacked pairs of layers that readily glide over one another. By far the most abundant members of this group is kaolinite, which is found in the coarse clay fraction of many soils of the world. The mineral endellite, with twice the water of kaolinite, is considered to be present in limited quantities in a few soils. It is generally accepted that kaolinite is predominantly the result of intensive weathering of feldspars and other common alumino silicates. As indicated by the formula, it contains approximately 46 % of SiO_2 and 40 % Al_2O_3. No isomorphous substitution is believed to occur either in the silica or alumina sheets, consequently, the composition is fairly uniform. Some rather pure deposits of kaolinite have formed as residual material on certain igneous rocks in humid subtropical regions.

Kaolinite is considered to be the most stable of all the clay minerals and is believed to form in environments where calcium, magnesium, potassium, and sodium are rapidly washed away during soil formation. It is overall neutral in charge.

7.3.2. Montmorrillonite Clay Mineral

This hydrous aluminum silicate mineral has been found in montmorrillonion France and got its name from two Frenchmen in 1847. Montmorrillonite is formed from 3 sheets. These are two sheets of silica are joined to a central alumina sheet in the planes of the apices of the silica tetrahedra. This is referred to as 2:1 layering. The three layers have a low net negative charge, and adjoining threesomes are loosely bonded together by a few cations, Na^+, K^+, Ca^{2+}, or Mg^{2+}. Because the bonding is weak, water can force the layers apart. This is what is known as an expanding clay, a major problems in engineering work.

The theoretical formula of montmorrillonite is $Al_4Si_8O_2(OH)_4.nH_2O$. Montmorrillonite is usually formed from the weathering of basic igneois rocks, it is believed that a plentiful supply of bases, particularly of magnesium and ferrous, is a requisite for the formation of minerals of this group. The overall charge of this clay mineral is negative.

7.3.3. Illite Clay Mineral

Illite has been proposed as a general term for the mica-like clay minerals by Grim *et al* [16]. The structure of the illite is similar to that of montmorrillonite except that there is always substantial replacement of silicon atoms by aluminum atoms in the tetrahedral layers, and potassium are between the layers, serving to balance the charges resulting the replacement and to tie the sheet units together, so that water and polar ions can enter between them and cause expansion. The basal spacing of 10Å remains unchanged. The structure of Illite mineral is similar to that of Montmorrillonite except that, on hydration, The lattice layers fail to expand because potassium ions perform a bridging action. Members of these complex group of clay minerals are especially abundant in soils that were formed from marine shales and limestones and that have not been subject to intense weathering. The substitution of aluminum (Al^{3+}) for silicon (Si^{4+}) in the tetrahedral layers increases the negative charge, which becomes neutralized by cations.

As a consequence of the 2:1 layering, and the attachment of cations, these clay minerals have less than do the 1:1 layered clay minerals. Montmorrillonite and illite have more silica, are less stable than kaolinite, are likely to whether to it.

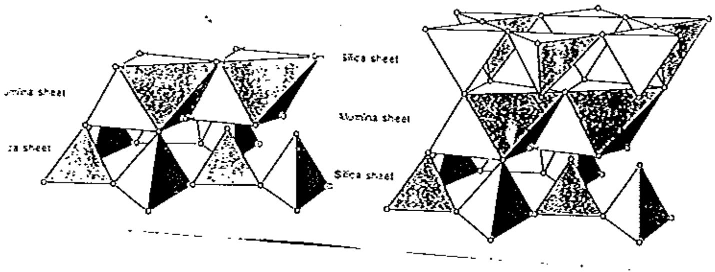
7.3.4. Chlorite and Vermiculite Clay Mineral

These two clay minerals have 2:1 layering similar to that of montmorrillonit and illite. They are common in surface deposits and soils, and readily alter to montmorrillonite, illite, or kaolinite. Still other clays are amorphous (e.g. allophan) and have indefinite chemical compositions.

An important consequence of the crystal structure if the clay minerals is the large number of sites at which the negatively charged anions and positively charged cations are not in electrostatic balance. There are sites with in each sheet within the hexagonal framework of tetrahedra and octahedra; there are sites between the sheets where they joined; and there are sites around the ragged edges of the crystals. Clays that have a considerable excess negative charge may act like acids in the presence of ground moisture [26-28].

Table 1. Approximate chemical composition of clay minerals

Mineral	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
Kaolinite	45-48	38-40	-	-	-	-	-	-
Montmorrillonite	42-55	0-28	0-30	0-0.5	0-3	0-25	0-0.5	0-3
Illite	50-56	18-31	2-5	0-0.8	0-2	1-4	4-7	0-1
Chlorite	31-33	18-20	-	-	-	35-38	-	-



Kaolinite Clay

Montimorrilonite Clay

Figure 1. Clay mineral structures.

8. EXPERIMENTAL

8.1. Reagents and Materials

A stock solution of 0.1 mol L^{-1} fluoride was prepared by dissolving known amount of NaF (Riedel-de Häen) in distilled water. Solutions of 1 x 10^{-5} -1 x 10^{-2} mol L^{-1} fluoride were prepared from the stock solution by serial dilution with distilled water for calibrating the electrode and for defluoridation studies.

Total ionic strength adjustment buffer (TISAB) was prepared by dissolving 57 mL of glacial acetic acid (Riedel-de Häen), 58 g of sodium chloride (Riedel-de Häen), 7 g of sodium citrate (NICE) and 2 g of EDTA (Pharmacos) in 500 mL of distilled water before dilution to volume (1 L), the pH was adjusted to 5.5 by adding 5 mol L^{-1} NaOH (NICE) solution.

8.2. Equipments

Harris standard magnetic stirrer was used for stirring the standard fluoride solutions, natural water samples and adsorbent. Heraceous centrifuge was used for separation of adsorbed fluoride from supernatant after end of contact time. An Orion combination fluoride ion-selective electrode (Model 96-09) with an Orion portable pH/ISE meter (Model 250) was used for the determination of fluoride. The pH of the solution was measured with Philips pH meter.

8.3 Fluoride Determination

8.3.1. Electrode Behaviour (Calibration Curve)

Aliquots (20 mL each) of 10^{-1}-10^{-6} mol L^{1} standard fluoride solutions were transferred separately into 100 mL polyproylene beakers and 5 mL of total ionic strength adjustor buffer (TISAB) were added to each solutions. The fluoride ion selective electrode was dipped into the stirred solution (25 mL : 20 mL standard fluoride solution and 5 mL TISAB). Constant potentials were recorded with 1 min. A calibration curve (E, mV versus log [F^-]) was constructed and used for the determination of fluoride in the sample solutions. All potential measurements were made at room temperature (20±2 °C).

8.3.2. Direct Potentiometry

A 20 mL aliquot of sample solution (or water sample) was transferred into a 100 mL polypropylene beaker and 5 mL of TISAB were added to it. The fluoride ion selective electrode was dipped into the stirred solution. A constant potential was recorded within 1 min. The fluoride ion concentration in the sample solution was determined from the calibration curve (E, mV vs log [F^-]). Alternatively, the concentration of fluoride in the sample solution can be calculated based on the single point calibration using equation (3) or by use of two standard solutions from equation (4).

8.3.3. Standard Addition Method

A 20 mL aliquot of the water sample was transferred into a 100 mL polypropylene beaker and a 5 mL TISAB was added to it. The fluoride ion selective electrode was dipped into the stirred solution and constant potential was recorded. This was followed by addition of 2 mL of $1x10^{-3}$ mol L^{-1} standard fluoride solution and potential was recorded. The concentration of the sample solution was calculated by equation (4).

8.4 Analysis of Fluoride Content of Natural Water Samples

Two sets of water samples were collected from the selected regions of Ethiopia. The first set was collected from high land regions of Ethiopia where the fluoride content was anticipated to be minimum and the second set was collected from Main Rift Valley regions of Ethiopia. The determination of fluoride content of natural water samples were made by using calibration curve for higher fluoride content and standard addition method for lower fluoride content. The places, sources, uses, and fluoride content of water samples are given in Tables 2 and 3. The places of water samples collection areas were shown in the map of Ethiopia (Figure 2). All water samples were collected in jarrycans, labeled, and brought to Addis Ababa, and kept at room temperature in the laboratory.

Table 2. Fluoride content of natural water samples

Place	Source	pH	F^- (mg L^{-1})	Remark/use
Sendefa	Pipe water	8.2	0.6	Drink/wash
D.B.	Borehole	7.8	0.2	Drink/wash
D.S.	Spring	7.8	0.4	Drink/wash
Shano	Borehole	8.3	0.2	Drink/wash
Shoa Robit	Hot-spring	7.5	1.8	Drink/wash
Kara Kori	Borehole	8.2	0.4	Drink/wash
Dejen	Pipe water	8.6	0.5	Drink/wash
Fiche	Spring	8.5	0.2	Drink/wash
Chancho	Spring	8.3	0.2	Drink/wash
Ambo	Pipe water	8.1	0.6	Drink/wash
Holota	Borehole	8.0	0.2	Drink/wash
Wolisso	Borehole	8.6	1.2	Drink/wash
Wolikite	Borehole	8.2	0.2	Drink/wash
Tullu Bollo	Hot-spring	8.6	0.6	Drink/wash
Sebeta	Borehole	8.5	0.7	Drink/wash
Robe	Pipe water	8.5	0.6	Drink/wash
Butajira	Spring	8.6	0.8	Drink/wash
Hossana	Borehole	8.4	1.5	Drink/wash
Assella	Pipe water	7.8	0.3	Drink/wash
Dodolla	Borehole	7.8	0.6	Drink/wash
Dhera	Pipe water	8.4	0.3	Drink/wash
Bushoftu	Pipe water	8.3	0.7	Drink/wash
Finfinne	pipe water	7.8	0.9	Drink/wash
Akaki	river	7.5	0.6	Drink/wash
Finfinne	river	8.6	2.0	Drink/wash
Kebena	river	8.4	0.2	Drink/wash

Table 3. Fluoride content of water samples collected from Ethiopia Main Rift Valley regions

Place	Source	pH	F^- (mg L^{-1})	Remark/use
Wonji Shoa	Borehole	8.3	12.8	Drink/wash
Mojjo	Pipe water	8.0	1.0	Drink/wash
Awasa Lake	Surface Water	8.8	9.5	Drink/wash
Abaya Lake	Surface Water	8.3	10.7	Drink/wash
Chamo Lake	Surface Water	9.0	10.4	Drink/wash
Bulbula	Borehole	8.4	6.0	Drink/wash

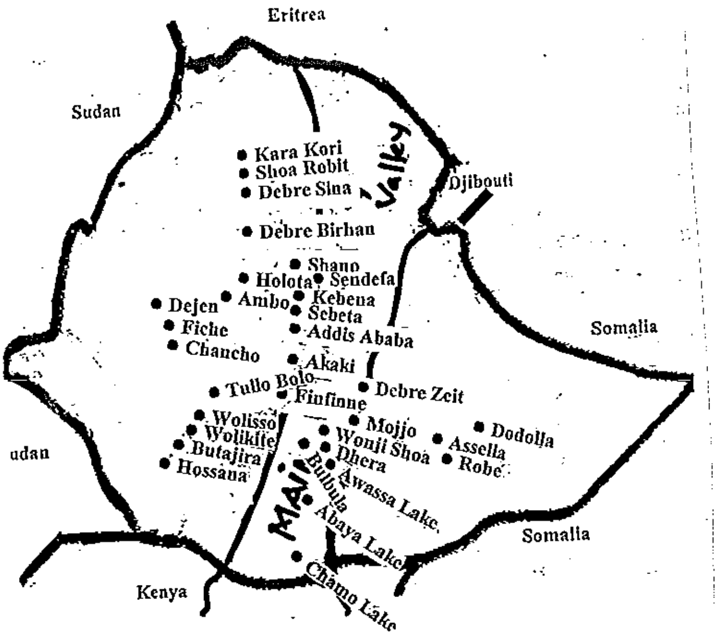


Figure 2. Map of Ethiopia showing the locations of water and clay samples collection areas.

8.5. Clay Samples

The clay samples were collected from nineteen different areas and the 20 th was fired clay. The clay samples were identified with their unique physical properties of plasticity using fingers. These nineteen areas were selected on the basis of low fluoride concentration in the ground waters. This was in accordance with what was reported by Redda *et al.* A WHO Expert Committee (1994) concluded that in high mountain areas the fluoride content of the soil is usually low. This is presumably due to the fluoride has been washed out of the top soil in high lands, and rivers and creeks had transported fluoride to the low lands, where it, due to evaporation, has enriched soil and ground waters. All clay samples were taken from the surface areas. The regions/locations of clay samples are shown in Figure 1.

The clay samples were collected in plastic bags, labeled, and brought to Addis Ababa for processing and defluoridation studying. All clay samples were finely ground in a Mortar with a Pestle and passed through a Sieve of approximately 0.1 mm pore size.The clay pot was bought from Gefersa on the Ambo road. The same procedure was used for the clay pot.

8.6. Defluoridation of Standard and Sample Solutions

A known weight (10-50 g) of the clay sample was (rapped into a cotton cloth) and transferred into a 1 L Pyrex beaker and a known volume (100-500 mL) of the standard fluoride solution (pH 5-6) or natural water samples (pH 7.5-8.5) was added to it. The mixture was allowed to stand for a known contact time (2-48 h) either with stirring or without stirring. At the end of contact time, the mixture was centrifuged for 10 min. The supernatant (the defluoridated water) was collected in a 1 L Pyrex beaker. A 20 mL aliquot of the supernatant (defluoridated water) was transferred into a 100 mL polypropylene beaker and 5 mL of TISAB was added to it. The fluoride ion selective electrode was dipped into the solution and a constant potential was recorded. The fluoride concentration was determined either by direct potentiometry (calibration method) or standard addition method.

The defluoridation of standard fluoride solution using clay was carried out as a function of mass of clay, volume of the fluoride solutions, and contact time of clay with fluoride solution, and pH. The pH of standard fluoride solutions which was 5.7 and 5.6 for 5.0 mg L^{-1} and 10.0 mg L^{-1}, respectively, was adjusted to 8.0 with 2 mol L^{-1} NaOH solution (encompassing the average pH range of most drinking water in Ethiopia Main Rift Valley). The pH of the standard fluoride solutions were measured before and after loading with the clay soils so as to propose the mechanism for clay and fluoride interaction. Defluoridation experiments were done in batch mode system.

The defluoridation of Wonji Shoa ground water (12.8 mg L^{-1} F^-) was similarly carried out using 6 clay soils. The pH of Wonji Shoa ground waters (12.8 mg L^{-1} F^{-1}) used for defluoridation study was 8.2. The studies were carried out as a function of mass of clay, volume of water and contact time. Defluoridation experiments were done in batch mode system.

8.7. Regeneration/Desorption Experiments

Regeneration/desorption experiments were carried out using 1% (w/v) NaOH solution. 500 g of Wolikite clay-fluoride complex was shaken with 1 L of 1% (w/v) NaOH solution and kept for 48 h. After 48 h the clay was separated from NaF solution then dried in the air for, again 48 h, crushed into powder, and sieved. The defluoridation with regenerated clay was done for three controlling factors, namely, mass, volume, and time.

8.8. Procedures and Parameters for Studying of Mass, Volume, and Time Effects of Clays

8.8.1. Effect of Mass

The fluoride removal capacities of 20 clay samples for a fixed volume of standard fluoride solution and natural water were investigated at constant period of contact time.

10-50 g of 20 clay samples were separately added to each of 5 and 10 mg L^{-1} standard fluoride solution (pH = 8) and ground water 12.8 mg L^{-1} F^{-1} (pH = 8.2); and the mixture was allowed to stand with stirring and/or non-stirring for an hour. At the end of a fixed period of contact time the fluoride was separated by centrifugation and filtration. 25 mL of supernatant solution was separated and then mixed with 5 mL of TISAB for fluoride analysis. The fluoride content was determined by direct potentiomerty and/or standard addition method using fluoride ion selective electrode.

8.8.2. Effect of Volume

The volume effect on fluoride removal capacities of clay was studied at constant mass of clay at fixed period of contact time. The volume effect on fluoride removal for 50 g of 20 clay samples was studied at various volume, viz., 100-500 mL of 5.0 and 10.0 mg L^{-1} standard fluoride solution at constant contact time of 1 h for both stirred and non-stirred solutions after the pH was adjusted to 8.0 with 2 mol L^{-1} NaOH solution (encompassing the average pH of most drinking water in fluoride rich areas). The same procedure was used for Wonji Shoa ground waters (12.80 mg F^- /L).

8.8.3. Effect of Time

The effect of contact time was investigated by adding a fixed amount of adsorbent (clay) to a constant volume of two different concentrations of standard fluoride solutions and one natural water sample at different period of contact time. After completion of the given contact time the mixture was separated.

The effect of time on fluoride removal with 50 g of 20 clay samples was evaluated for 500 mL of 5.0 and 10.0 mg L^{-1} standard fluoride solution at a contact time of 2-48 h for both stirred and non-stirred solutions after the pH was adjusted to 8.0 with 2 mol L^{-1} solution (encompassing the average pH of most drinking water in Ethiopia Main Rift Valley where excessive fluoride exists). Similar experimental procedure was used for Wonji Shoa ground water (12.8 mg^{1} L) for defluoridation.

8.8.4. Effect of PH

The effect of pH was studied by adding a fixed amount of adsorbent (clay) to a constant volume of 10 mg L^{-1} standard fluoride solution at constant contact time. After a constant contact of an hour the supernatant was separated.

50 g of 20 clay samples were separately loaded to four beakers containing 500 mL of 10.0 mg L^{-1} standard fluoride solution with different pH, viz., 3, 5, 7 and 9 at constant contact time of 1 h for both stirred and non-stirred solutions. The pH of standard fluoride solution was adjusted with 1 mol L^{-1} HCl and 2 mol L^{-1} NaOH solution (the pH of 10.0 mg L^{-1} standard fluoride solution was 5.6).

8.9. Fluoride Adsorbed, Removal Efficiency and Defluoridation Capacity

The residual fluoride concentration in the standard was calculated by the formula derived from the Nernst equation: $E_S - E_X = \Delta E = S \log C_X/C_S$

which can be rearranged to be: $C_X = C_S\ 10^{\Delta E/S}$

where C_X = concentration of the analyte after time t

C_S = initial concentration of standard solution

E_X = electrode potential of the analyte after time t

E_S = electrode potential of the standard solution

S = slope

The fluoride removal efficiency and the fluoride adsorbed in a given period of contact time were calculated as follows:

The amount of fluoride adsorbed/removed = $C_o - C_t$ and;

percentage of removal efficiency = $(C_o - C_t)x100/C_o$

where C_o = initial concentration of the fluoride in the solution in mg L^{-1} at t = 0

C_t = final concentration of the fluoride in solution in mg L^{-1} after t contact time

Defluoridation capacity of clays was determined using the following relationship:

$$\text{Defluoridation capacity in mg/kg} = \text{mg}\,F^{-1}\text{/kg clay} = \frac{\text{mg of } F^{-1} \text{ removed}}{\text{amount of clay in g}} \times 1000$$

9. RESULTS AND DISCUSSION

9.1. Effect of Mass

The results shown in Tables 4-6 and Figures 3-7 indicate that the residual fluoride concentrations in both standard fluoride solutions and ground water samples decreased with the increased amounts of clays. Among the adopted clay for defluoridation the fired clay chips was the least defluoridating agent (10 mg L^{-1} F^{-1} come down to 3.0 mg L^{-1}) presumably due to the effect of firing, however, Wolikite clay was found to be the most efficient (10 mg L^{-1} F^- come down to 1.0 mg L^{-1} F^-).

The observed residual fluoride concentrations were between 2.3-0.8 mg L^{-1} for 5.0 mg L^{-1} initial standard fluoride concentration and between 3.0-1.0 mg L^{-1} for 10.0 mg L^{-1} initial standard fluoride concentration. The result obtained showed that residual fluoride concentration decreases with increasing mass of the adsorbent. This is most likely due to an increase in active sites. This indicates that the removal of fluoride from ground waters is dependent upon mass of clay used.

Table 4. Effect of mass of 20 clay samples on 500 mL of 5.0 mg L^{-1} standard fluoride solution at constant contact time of 1 h for both stirred and non-stirred solutions after the pH was adjusted to 8.0 with 2 mol L^{-1} NaOH solution.

Clay type	Mass of clay, g	10	20	30	40	50
	S, residual F^-, mg L^{-1}	2.92	2.76	2.62	2.53	2.35
	NS, residual F^-, mg L^{-1}	2.87	2.75	2.56	2.47	2.34
	%F^- removed	41.6	45	47	49.4	53
Gullalle	S, residual F^-, mg L^{-1}	2.16	1.72	1.54	1.42	1.37
	NS, residual F^-, mg L^{-1}	2.1	1.7	1.53	1.38	1.3
	%F^- removed	56.8	65.6	69.2	71.6	72.6

RBB	S, residual F^-, mg L^{-1}	1.8	1.7	1.25	1.1	1
	NS, residual F^-, mg L^{-1}	1.9	1.7	1.45	1.4	1.2
	%F^- removed	64	68	75	78	80
WBB	S, residual F^-, mg L^{-1}	1.85	1.65	1.3	1.2	1.1
	NS, residual F^-, mg L^{-1}	1.75	1.6	1.25	1.1	1.08
	%F^- removed	63	67	74	76	78
Shano	S, residual F^-, mg L^{-1}	2.3	2	1.9	1.7	1.5
	NS, residual F^-, mg L^{-1}	2.2	2	1.78	1.7	1.48
	%F^- removed	54	60	62.2	66	70
Debre Sina	S, residual F^-, mg L^{-1}	2	1.8	1.6	1.5	1.4
	NS, residual F^-, mg L^{-1}	1.9	1.75	1.6	1.45	1.3
	%F^- removed	60	64	68	70	72
Kara Kori	S, residual F^-, mg L^{-1}	3.2	2.8	2.1	1.8	1.5
	NS, residual F^-, mg L^{-1}	3.1	2.6	2	1.7	1.4
	%F^- removed	36	44	58	64	70
Dejen	S, residual F^-, mg L^{-1}	1.9	1.8	1.6	1.5	1.4
	NS, residual F^-, mg L^{-1}	1.85	1.7	1.56	1.4	1.3
	%F^- removed	62	64	68	70	72
Fiche	S, residual F^-, mg L^{-1}	2	1.85	1.76	1.5	1.4
	NS, residual F^-, mg L^{-1}	1.9	1.75	1.65	1.45	1.28
	%F^- removed	60	63	66	70	72
Chancho	S, residual F^-, mg L^{-1}	1.54	1.42	1.3	1.25	1.1
	NS, residual F^-, mg L^{-1}	1.5	1.38	1.26	1.15	1.06
	%F^- removed	69.2	71.6	73.9	75	78
Ambo	S, residual F^-, mg L^{-1}	2	1.9	1.78	1.62	1.54
	NS, residual F^-, mg L^{-1}	1.9	1.85	1.78	1.6	1.48
	%F^- removed	60	62	63.6	67.6	69.2
Holota	S, residual F^-, mg L^{-1}	1.76	1.62	1.48	1.36	1.26
	NS, residual F^-, mg L^{-1}	1.7	1.6	1.5	1.34	1.25
	%F^- removed	64.8	67.6	70.4	72.8	74.8
Wolisso	S, residual F^-, mg L^{-1}	1.92	1.74	1.62	1.48	1.31
	NS, residual F^-, mg L^{-1}	1.88	1.71	1.58	1.45	1.27
	%F^- removed	61.8	65.1	67.6	70.4	73.8
Wolikite	S, residual F^-, mg L^{-1}	1.48	1.35	1.11	0.97	0.81
	NS, residual F^-, mg L^{-1}	1.47	1.33	1.08	0.95	0.8
	%F^- removed	71.5	73	77.8	80.6	83.8
Hossana	S, residual F^-, mg L^{-1}	2.3	2.1	1.91	1.75	1.61
	NS, residual F^-, mg L^{-1}	2.22	2.07	1.88	1.72	1.56
	%F^- removed	54.4	58.1	61.9	65	67.8

Tullu Bollo	S, residual F^-, mg L^{-1}	2.3	2.08	1.99	1.69	1.58
	NS, residual F^-, mg L^{-1}	2.25	2.06	1.96	1.67	1.55
	%F^- removed	58.4	60.2	64	66.2	68.4
Butajira	S, residual F^-, mg L^{-1}	1.95	1.88	1.78	1.66	1.52
	NS, residual F^-, mg L^{-1}	1.92	1.84	1.73	1.62	1.48
	%F^- removed	61	62.4	64.4	66.8	69.8
Robe	S, residual F^-, mg L^{-1}	1.98	1.87	1.76	1.64	1.41
	NS, residual F^-, mg L^{-1}	1.92	1.84	1.73	1.62	1.4
	%F^- removed	60.4	62.6	64.8	67.2	71.8
Assella	S, residual F^-, mg L^{-1}	1.92	1.62	1.36	1.25	1.2
	NS, residual F^-, mg L^{-1}	1.9	1.55	1.33	1.22	1.1
	%F^- removed	61.6	67.6	72.8	75	76
Dodolla	S, residual F^-, mg L^{-1}	1.77	1.48	1.36	1.25	1.16
	NS, residual F^-, mg L^{-1}	1.75	1.45	1.33	1.22	1.12
	%F-removed	64.7	70.4	72.8	75	76.6

Table 5. Effect of mass of 20 sample soils on 500 mL of 10.0 mg L^{-1} standard fluoride solution at constant contact time of 1 h of both stirred and non-stirred solutions after the pH was adjusted to 8.0 by 2 mol L^{-1} NaOH solution

Clay type	Mass of clay, g	10	20	30	40	50
Fired	S, residual F^-, mg L^{-1}	3.72	3.53	3.4	3.24	3.12
	NS, residual F^-, mg L^{-1}	3.6	3.46	3.3	3.16	3.08
	%F^- removed	62.8	64.8	66	67.6	68.8
Gullalle	S, residual F^-, mg L^{-1}	3.4	2.8	2.4	2.2	2.1
	NS, residual F^-, mg L^{-1}	3.3	2.7	2.3	2.2	2.1
	%F^- removed	66.3	72	76.3	78	78.8
RBB	S, residual F^-, mg L^{-1}	2.4	1.75	1.66	1.58	1.48
	NS, residual F^-, mg L^{-1}	2.9	2.6	2.3	2.1	1.85
	%F^- removed	76	82	83.4	84.2	85.2
WBB	S, residual F^-, mg L^{-1}	2.7	2.5	2.3	2.1	1.9
	NS, residual F^-, mg L^{-1}	2.6	2.4	2.2	2	1.85
	%F^- removed	73	75	77	79	81
Shano	S, residual F^-, mg L^{-1}	3.5	3.3	3	2.8	2.5
	NS, residual F^-, mg L^{-1}	3.48	3.26	2.95	2.7	2.5
	%F^- removed	65	67	70	72	75
Debre Sina	S, residual F^-, mg L^{-1}	3.1	2.8	2.6	2.4	2.2
	NS, residual F^-, mg L^{-1}	3	2.7	2.4	2.3	2.1
	%F^- removed	69	72	74	76	78

Kara Kori	S, residual F$^-$, mg L^{-1}	4.2	3.4	2.9	2.5	2.4
	NS, residual F$^-$, mg L^{-1}	4.1	3.2	2.8	2.3	2
	%F$^-$ removed	58	66	71	75	76
Dejen	S, residual F$^-$, mg L^{-1}	2.7	2.4	2.2	2	1.9
	NS, residual F$^-$, mg L^{-1}	2.6	2.4	2.1	1.95	1.8
	%F$^-$ removed	73	76	78	80	81
Fiche	S, residual F$^-$, mg L^{-1}	2.8	2.6	2.4	2.2	1.8
	NS, residual F$^-$, mg L^{-1}	2.65	2.4	2.2	2.1	1.7
	%F$^-$ removed	72	74	76	78	82
Chancho	S, residual F$^-$, mg L^{-1}	2.2	2.05	1.88	1.75	1.6
	NS, residual F$^-$, mg L^{-1}	2.15	1.95	1.8	1.64	1.5
	%F$^-$ removed	78	79.5	81.2	82.5	84
Ambo	S, residual F$^-$, mg L^{-1}	2.7	2.5	2.38	2	1.85
	NS, residual F$^-$, mg L^{-1}	2.67	2.45	2.36	2.04	1.9
	%F$^-$ removed	73	75	76.2	80	81.5
Holota	S, residual F$^-$, mg L^{-1}	2.5	2.31	2	1.84	1.58
	NS, residual F$^-$, mg L^{-1}	2.48	2.25	2.06	1.9	1.75
	%F$^-$ removed	75	76.9	80	81.6	84.2
Wolisso	S, residual F$^-$, mg L^{-1}	2.75	2.5	2.3	2.11	1.93
	NS, residual F$^-$, mg L^{-1}	2.67	2.45	2.22	2.02	1.85
	%F$^-$ removed	72.5	74.9	77	78.9	80.7
Wolikite	S, residual F$^-$, mg L^{-1}	2.11	1.94	1.56	1.45	1.11
	NS, residual F$^-$, mg L^{-1}	2.08	1.9	1.53	1.43	1.09
	%F$^-$ removed	78.9	81.6	84.4	85.5	88.9
Hossana	S, residual F$^-$, mg L^{-1}	3.22	2.98	2.72	2.5	2.3
	NS, residual F$^-$, mg L^{-1}	3.16	2.9	2.66	2.42	2.25
	%F$^-$ removed	67.8	70.2	72.8	75	77
Tullu Bollo	S, residual F$^-$, mg L^{-1}	3.23	3	2.84	2.7	2.5
	NS, residual F$^-$, mg L^{-1}	3.18	2.95	2.69	2.46	2.28
	%F$^-$ removed	67.7	70	71.6	73	75
Butajira	S, residual F$^-$, mg L^{-1}	2.68	2.54	2.46	2.38	2.2
	NS, residual F$^-$, mg L^{-1}	2.62	2.5	2.42	2.36	2.1
	%F$^-$ removed	73.2	74.6	75.4	76.2	78
Robe	S, residual F$^-$, mg L^{-1}	2.8	2.65	2.53	2.47	2.4
	NS, residual F$^-$, mg L^{-1}	2.78	2.62	2.5	2.45	2.36
	%F$^-$ removed	72	73.5	74.7	75.3	76
Assella	S , residual F$^-$, mg L^{-1}	2.75	2.62	2.5	2.46	2.35
	NS, residual F$^-$, mg L^{-1}	2.7	2.6	2.48	2.42	2.3
	%F$^-$ removed	72.5	74	75	75.4	76.5

Dodolla	S, residual F^-, mg L^{-1}	2.5	2.1	1.95	1.78	1.65
	NS, residual F^-, mg L^{-1}	2.42	2.02	1.88	1.7	1.6
	%F^- removed	75	79	80.5	82.2	83.5

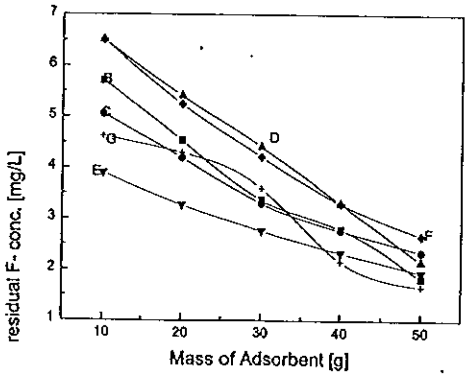


Figure 3. Residual fluoride concentration of standard fluoride solution (10 mg L^{-1}) as a function of mass of of fired (B), Gullalle (C), RBB (D), WBB (E), and Shano (F) clays at constant contact time of 1 h.

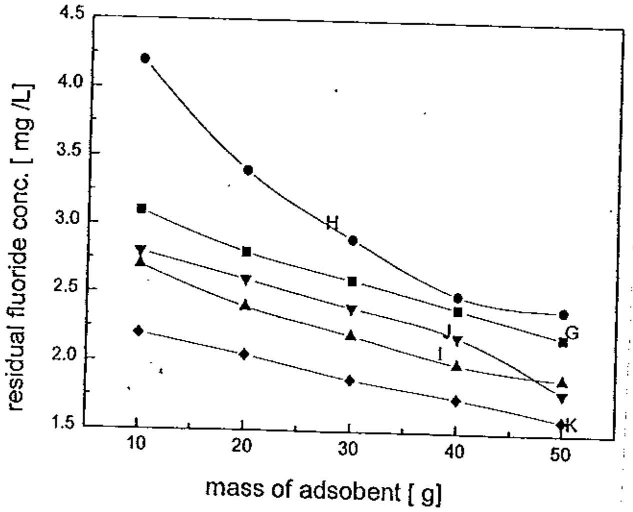


Figure 4. Residual fluoride concentration of standard fluoride solution (10 mg L^{-1}) as a function of mass of Debre Sina (G), Karakori (H), Dejen (I), Fiche (J), and Chancho (K) clays at constant contact time of 1 h.

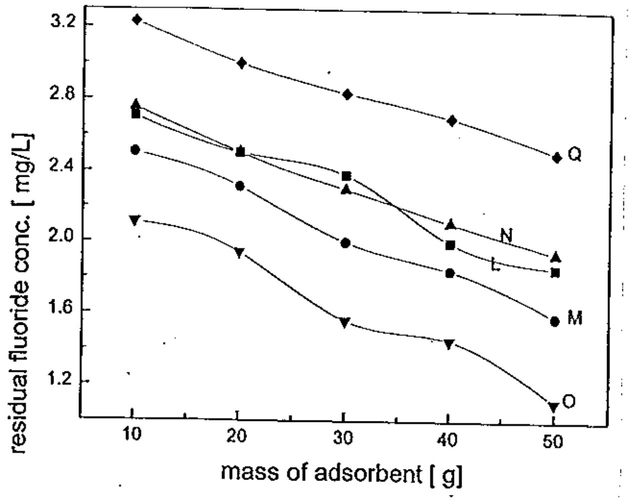


Figure 5. Residual fluoride concentration of standard fluoride solution (10 mg L^{-1}) as a function of mass of Ambo (L), Holota (M), Wolisso (N) , Wolikite (O), and Hossana (P) clays at constant contact time of 1 h.

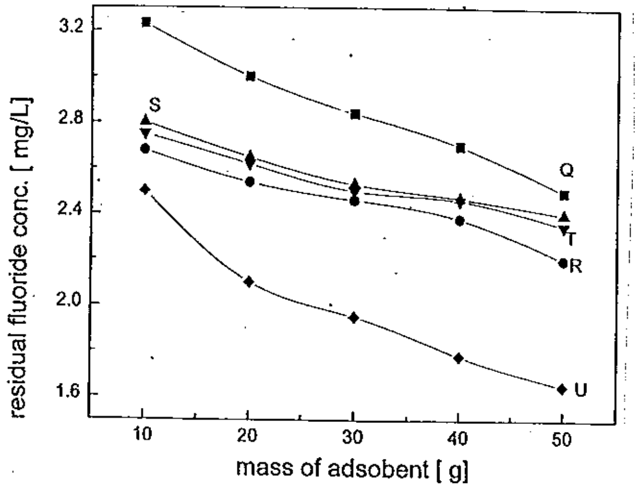


Figure 6. Residual fluoride concentration of standard fluoride solution (10 mg L^{-1}) as a function of mass of Tullu Bollo (Q), Butajira (R), Robe (S), Assella (T), and Dodolla (U) clays at constant contact time of 1 h.

9.2. Effect of Volume

The result obtained showed that residual fluoride concentration was increased with increased volume of particular standard fluoride solution and Wonji Shoa groundwater as shown in Tables 7-9 and Figures 8-12, respectively. The substantial decrease in the fluoride removal is due to the decrease in the active sites in the clays. The observed residual fluoride concentrations were between 2.4-0.9 mg L^{-1} for 5.0 mg L^{-1} initial standard fluoride solution and between 3.0-0.5 mg L^{-1} for 10.0 mg L^{-1} initial standard fluoride solution. This implies that the residual fluoride concentrations observed for various volumes, viz., 100-500 mL of 5 and 10 mg $F^- L^{-1}$ were brought down to below the recommended limit of fluoride concentration. Therefore, the fluoride removal efficiency of clays is considerably affected by volume of fluoride solution.

Table 7. Effect of volume of 5.0 mg L^{-1} standard fluoride solution on fluoride removal with 50 g of 20 clay samples at constant contact time of 1 h for both stirred and non-stirred solutions.

Clay type	Volume of solution, mL	100	200	300	400	500
Fired	S, residual F^-, mg L^{-1}	1.62	1.8	1.9	2.2	2.4
	NS, residual F^-, mg L^{-1}	1.6	1.75	1.8	2	2.35
	%F^- removed	67.6	64	60	56	52
Gullalle	S, residual F^-, mg L^{-1}	0.62	0.75	0.96	1.4	1.5
	NS, residual F^-, mg L^{-1}	0.63	0.75	0.95	1.5	1.45
	%F^- removed	87.7	85	80.9	72	70.2
RBB	S, residual F^-, mg L^{-1}	0.6	0.9	1.05	1.2	1.25
	NS, residual F^-, mg L^{-1}	0.55	0.85	1	1.1	1.2
	%F^- removed	88	82	79	76	75
WBB	S, residual F^-, mg L^{-1}	0.6	0.75	0.96	1.1	1.3
	NS, residual F^-, mg L^{-1}	0.6	0.7	0.9	1.05	1.2
	%F^- removed	88	85	80.8	78	74
Shano	S, residual F^-, mg L^{-1}	0.6	0.8	1	1.2	1.3
	NS, residual F^-, mg L^{-1}	0.62	0.75	0.9	0.98	1.2
	%F^- removed	88	82	80	76	74
Debre Sina	S, residual F^-, mg L^{-1}	0.6	0.7	0.85	1.1	1.2
	NS, residual F^-, mg L^{-1}	0.6	0.65	0.8	0.98	1.1
	%F^- removed	88	86	83	78	76

Kara Kori	S, residual F$^-$, mg L^{-1}	1.2	1.28	1.36	1.4	1.56
	NS, residual F$^-$, mg L^{-1}	1.1	1.25	1.32	1.38	1.52
	%F$^-$ removed	76	74.4	72:8	72	68.8
Dejen	S, residual F$^-$, mg L^{-1}	0.76	1.1	1.2	1.4	1.5
	NS, residual F$^-$, mg L^{-1}	0.66	1	1.1	1.3	1.5
	%F$^-$ removed	86	78	76	72	70
Fiche	S, residual F$^-$, mg L^{-1}	0.65	0.96	1.08	1.2	1.3
	NS, residual F$^-$, mg L^{-1}	0.58	0.85	1	1.1	1.24
	%F$^-$ removed	87	80.8	78.4	76	74
Chancho	S, residual F$^-$, mg L^{-1}	0.45	0.56	0.58	0.65	0.92
	NS, residual F$^-$, mg L^{-1}	0.42	0.54	0.56	0.62	0.9
	%F$^-$ removed	91	88.8	88.4	87.8	81.6
Ambo	S, residual F$^-$, mg L^{-1}	0.6	0.97	1.2	1.4	1.5
	NS, residual F$^-$, mg L^{-1}	0.58	0.94	1.12	1.33	1.43
	%F$^-$ removed	88	80.6	76	72	70
Holota	S, residual F$^-$, mg L^{-1}	0.42	0.69	0.98	1.16	1.26
	NS, residual F$^-$, mg L^{-1}	0.4	0.67	0.95	1.12	1.22
	%F$^-$ removed	91.6	86.2	80.5	76.8	74.8
Wolisso	S, residual F$^-$, mg L^{-1}	0.78	1.22	1.45	1.62	1.75
	NS, residual F$^-$, mg L^{-1}	0.76	1.2	1.45	1.6	1.72
	%F$^-$ removed	84.4	75.6	71	67.6	65
Wolikite	S, residual F$^-$, mg L^{-1}	0.35	0.53	0.63	0.75	0.89
	NS, residual F$^-$, mg L^{-1}	0.34	0.52	0.63	0.73	0.87
	%F$^-$ removed	93	89.4	87.4	85	82.2
Hossana	S, residual F$^-$, mg L^{-1}	0.88	1.35	1.42	1.66	1.78
	NS, residual F$^-$, mg L^{-1}	0.86	11.34	1.46	1.62	1.84
	%F$^-$ removed	82.4	73	71.6	66.8	62.4
Tullu Bollo	S, residual F$^-$, mg L^{-1}	1.36	1.48	1.62	1.8	1.92
	NS, residual F$^-$, mg L^{-1}	1.34	1.45	1.6	1.75	1.88
	%F$^-$ removed	72.8	70.4	67.6	64	61.6
Butajira	S, residual F$^-$, mg L^{-1}	0.63	0.82	0.97	1.15	1.25
	NS, residual F$^-$, mg L^{-1}	0.62	0.78	0.94	1.11	1.22
	%F$^-$ removed	87.2	84.6	80.6	77	75
Robe	S, residual F$^-$, mg L^{-1}	0.67	0.86	1	1.25	1.36
	NS, residual F$^-$, mg L^{-1}	0.66	0.82	0.95	1.22	1.34
	%F$^-$ removed	87.4	82.8	80	75	72.8
Assella	S, residual F$^-$, mg L^{-1}	0.68	0.92	1.2	1.3	1.4
	NS, residual F$^-$, mg L^{-1}	0.7	0.9	1.1	1.2	1.35
	%F$^-$ removed	86.4	81.6	76	74	72

Dodolla	S, residual F^-, mg L^{-1}	0.59	0.75	0.98	1.2	1.25
	NS, residual F^-, mg L^{-1}	0.58	0.74	0.96	1.1	1.2
	%F^- removed	88.2	85	80.4	76	75

Table 8. Effect of volume of 10.0 mg L^{-1} standard fluoride solution on fluoride removal with 50 g of 20 clay samples at constant contact time of 1 h for both stirred and non-stirred solutions.

Clay type	Volume of solution, mL	100	200	300	400	500
Fired	S, residual F^-, mg L^{-1}	3.12	3.24	3.4	3.53	3.72
	NS, residual F^-, mg L^{-1}	3.1	3.2	3.36	3.5	3.7
	%F^- removed	68.8	67.6	66	65.47	62.8
Gullalle	S, residual F^-, mg L^{-1}	0.92	1.2	1.5	1.9	2.3
	NS, residual F^-, mg L^{-1}	0.9	1.1	1.38	1.9	2.1
	%F^- removed	90.8	88.2	84.9	80.7	77
RBB	S, residual F^-, mg L^{-1}	0.8	1.2	1.3	1.38	1.5
	NS, residual F^-, mg L^{-1}	0.75	1.2	1.25	1.36	1.46
	%F^- removed	92	88	87	86.2	85
WBB	S, residual F^-, mg L^{-1}	0.8	1.1	1.5	1.8	2
	NS, residual F^-, mg L^{-1}	0.7	1	1.4	1.7	1.9
	%F^- removed	92	89	85	82	80
Shano	S, residual F^-, mg L^{-1}	1.2	1.36	1.8	2.4	2.48
	NS, residual F^-, mg L^{-1}	1.1	1.34	1.75	2.38	2.45
	%F^- removed	88	86.4	82	76	75.2
Debre Sina	S, residual F^-, mg L^{-1}	0.9	1.1	1.25	1.5	1.8
	NS, residual F^-, mg L^{-1}	0.95	1	1.2	1.45	1.7
	%F^- removed	91	89	87.5	85	82
Kara Kori	S, residual F^-, mg L^{-1}	1.4	1.5	1.85	2.32	2.45
	NS, residual F^-, mg L^{-1}	1.25	1.48	1.9	2.3	2.4
	%F^- removed	86	85	80.5	76.8	75.5
Dejen	S, residual F^-, mg L^{-1}	1	1.4	1.7	1.9	2
	NS, residual F^-, mg L^{-1}	0.95	1.4	1.6	1.8	1.95
	%F^- removed	90	86	83	81	80
Fiche	S, residual F^-, mg L^{-1}	0.94	1.28	1.48	1.82	1.96
	NS, residual F^-, mg L^{-1}	0.91	1.2	1.44	1.65	1.9
	%F^- removed	90.6	87.2	85.2	81.8	80.4
Chancho	S, residual F^-, mg L^{-1}	0.99	1.24	1.36	1.42	1.8

Chancho	S, residual F^-, mg L^{-1}	0.99	1.24	1.36	1.42	1.8
	NS, residual F^-, mg L^{-1}	0.96	1.22	1.3	1.4	1.75
	%F^- removed	90.1	87.6	86.4	85.8	82
Ambo	S, residual F^-, mg L^{-1}	0.64	1.1	1.3	1.5	1.64
	NS, residual F^-, mg L^{-1}	0.62	1.04	1.24	1.48	1.63
	%F^- removed	93.6	89	87	85	83.6
Holota	S, residual F^-, mg L^{-1}	0.59	0.99	1.26	1.5	1.63
	NS, residual F^-, mg L^{-1}	0.58	0.96	1.24	1.45	1.6
	%F^- removed	94.1	90.1	87.4	85	83.7
Wolisso	S, residual F^-, mg L^{-1}	1.2	1.36	1.48	1.64	1.73
	NS, residual F^-, mg L^{-1}	1.16	1.32	1.4	1.62	1.7
	%F^- removed	88	86.4	85.2	83.6	82.7
Wolikite	S, residual F^-, mg L^{-1}	0.5	0.75	0.87	1.02	1.2
	NS, residual F^-, mg L^{-1}	0.48	0.72	0.86	1.01	1.24
	%F^- removed	95	92.5	91.5	89.8	88
Hossana	S, residual F^-, mg L^{-1}	1.56	1.72	1.93	2.2	2.46
	NS, residual F^-, mg L^{-1}	1.56	1.7	1.91	2.18	2.42
	%F^- removed	84.4	82.8	80.7	78	75.4
Tullu Bollo	S, residual F^-, mg L^{-1}	1.64	1.8	1.93	2.11	2.6
	NS, residual F^-, mg L^{-1}	1.63	1.8	1.94	2.1	2.28
	%F^- removed	83.6	82.8	80.7	78.9	77
Butajira	S, residual F^-, mg L^{-1}	0.92	1.15	1.38	1.64	1.8
	NS, residual F^-, mg L^{-1}	0.9	1.11	1.33	1.5	1.74
	%F^- removed	90.8	88.5	86.2	83.6	82
Robe	S, residual F^-, mg L^{-1}	1.1	1.25	1.44	1.85	2.4
	NS, residual F^-, mg L^{-1}	1.08	1.24	1.42	1.8	2.36
	%F^- removed	89	87.5	85.6	81.5	76
Assella	S, residual F^-, mg L^{-1}	1.05	1.26	1.4	1.75	2.3
	NS, residual F^-, mg L^{-1}	1	1.25	1.38	1.68	2.2
	%F^- removed	88.5	87.6	86	82.5	77
Dodolla	S, residual F^-, mg L^{-1}	1	1.2	1.36	1.6	2
	NS, residual F^-, mg L^{-1}	1	1.1	1.34	1.52	1.9
	%F^- removed	90	88	86.4	84	80

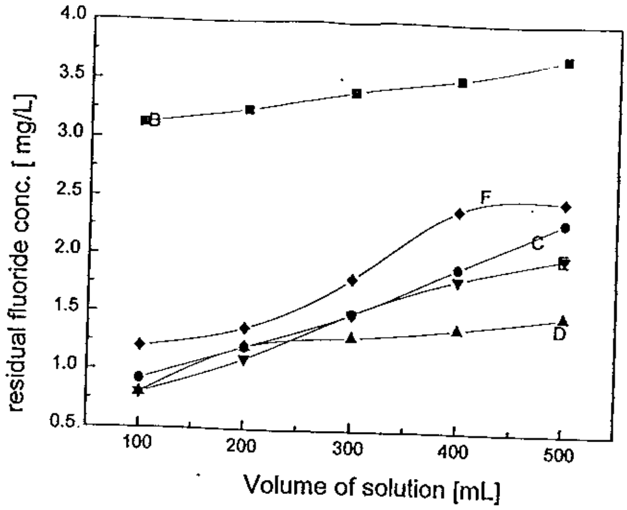


Figure 8. Residual fluoride concentration as a function of volume of standard fluoride solution (10 mg F^-/L) on contact with 50 g of Fired (B), Gullalle (C), RBB (D), WBB (E), and Shano (F) clays at constant contact time of 1 h.

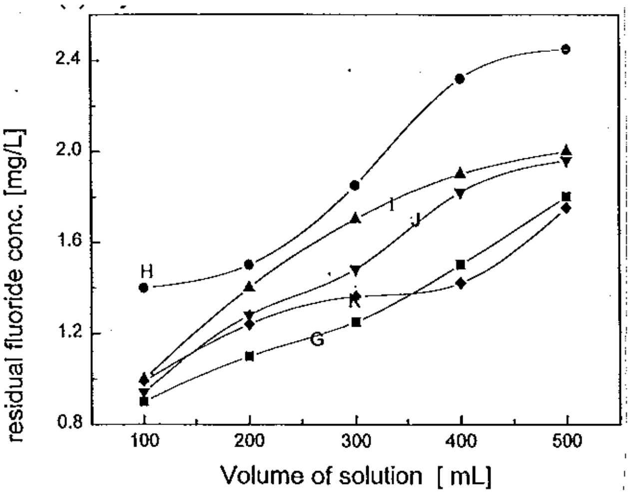


Figure 9. Residual fluoride concentration as a function of volume of standard fluoride solution (10 mg F^-/L) on contact with 50 g of Debre Sina (G), Karakori (H), Dejen (I), Fiche (J), and Chancho (K) clays at constant contact time of 1 h..

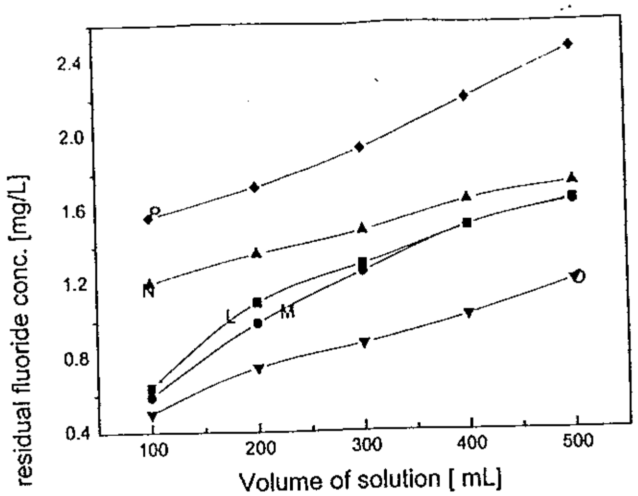


Figure 10. Residual fluoride concentration as a function of volume of standard fluoride solution (10 mg F^-/L) on contact with 50 g of Ambo (L), Holota (M), Wolisso (N),Wolikite (O), and Hossana (P) clays at constant contact time of 1 h..

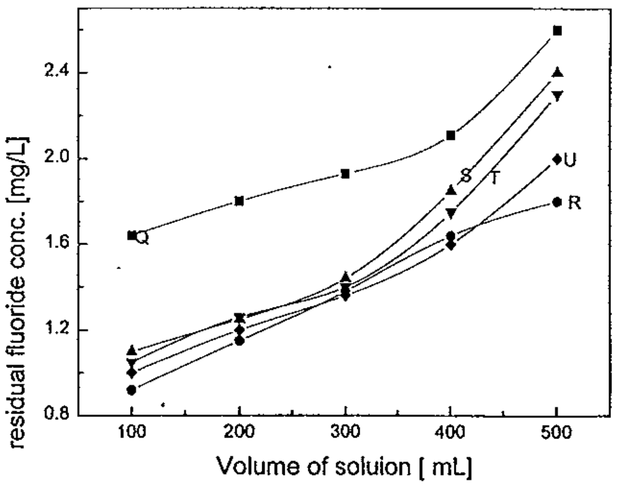


Figure 11. Residual fluoride concentration as a function of volume of standard fluoride solution (10 mg F^-/L) on contact with 50 g of Tullu Bollo (Q), Butajira (R), Robe (S), Assella (T), and Dodolla (U) clays. at constant contact time of 1 h.

Table 9. Effect of volume of Wonji Shoa ground water (12.8 mg F^- L^{-1}) on fluoride remove with 50 g of 6 clay samples at constant contact time of 1 h for both stirred and non-stirred solutions.

Clay type	Volume of solution, mL	100	200	300	400	500
RBB	S, residual F^-, mg L^{-1}	0.70	0.92	1.20	1.38	1.65
	NS, residual F^-, mg L^{-1}	0.67	0.87	1.14	1.35	1.60
	%F^- removed	94.2	92.4	90.20	88.5	86.2
Gullalle	S, residual F^-, mg L^{-1}	0.65	0.90	1.40	1.65	2.32
	NS, residual F^-, mg L^{-1}	0.62	0.87	1.35	1.60	2.30
	%F^- removed	94.6	92.5	88.4	86.2	80.7
Ambo	S, residual F^-, mg L^{-1}	0.84	1.08	1.52	1.80	2.15
	NS, residual F^-, mg L^{-1}	0.80	1.03	1.46	1.72	2.05
	%F^- removed	93.0	91.0	87.3	85.0	82.1
Holota	S, residual F^-, mg L^{-1}	0.42	0.60	0.70	0.99	1.40
	NS, residual F^-, mg L^{-1}	1.40	1.56	0.66	0.95	1.35
	%F^- removed	96.5	95.0	94.0	91.7	88.4
Chancho	S, residual F^-, mg L^{-1}	0.99	1.28	1.66	2.14	2.52
	NS, residual F^-, mg L^{-1}	0.96	1.25	1.62	2.1	2.50
	%F^- removed	91.7	89.3	86.0	82.0	79.0
Wolikite	S, residual F^-, mg L^{-1}	0.35	0.60	0.84	1.04	1.40
	NS, residual F^-, mg L^{-1}	0.32	0.58	0.80	1.0	1.38
	%F^- removed	97.0	95.0	93.0	91.4	88.8

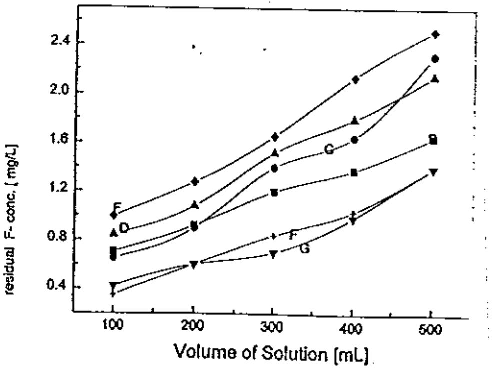


Figure 12. Residual fluoride concentration as a function of volume of Wonji Shoa groundwater (12.80 mg F^- L^{-1}) on contact with 50 g RBB (B), Gullalle (C), Ambo (D), Holota (E), Chancho (F), and Wolikite (G) clays at constant contact time of 1 h.

9.3. Effect of Time

The result obtained showed that residual fluoride concentration decreases with increasing periods of contact as shown in Tables 10-12 and Figures 13-17. The fluoride removal capacities of clays are significantly affected by period of contact time. The residual fluoride concentration came down to 0.1 mg L^{-1} from 5.0 mg L^{-1} initial fluoride concentration and to 0.2 mg L^{-1} from 10.0 mg L^{-1} initial standard fluoride concentration after 48 h of storage time. This indicates that the residual fluoride concentration observed for different storage time, viz., 2 - 48 h of 5 and 10 mg L^{-1} standard fluoride solutions is brought down to WHO maximum permissible level (1 mg L^{-1}) of fluoride concentration after 24 h contact time for most of the adopted clays except fired clay chips. Fired clay was found to be the least efficient, but Wolikite clay was found to be the most efficient.

Table 10. Effect of contact time on the fluoride removal with 50 g of 20 clay samples from 500 mL of 5.0 mg L^{-1} standard fluoride solution for both stirred and non-stirred solutions. (V:W = 10:1; residual fluoride concentration in mg/L)

Clay type	Contact time, h	2	4	6	8	12	24	48
Fired	S, residual F^-, mg L^{-1}	2.25	2.1	2	1.9	1.75	1.55	1.25
	NS, residual F^-, mg L^{-1}	2.2	2	1.95	1.88	1.72	1.53	1.2
	%F^- removed	55	58	60	62	65	69	75
Gullalle	S, residual F^-, mg L^{-1}	1.4	1.3	1.2	1.2	0.9	0.9	0.8
	NS, residual F^-, mg L^{-1}	1.38	1.26	1.2	1.06	0.9	0.88	0.8
	%F^- removed	71.7	74	75.6	78.7	82	82	83.7
RBB	S, residual F^-, mg L^{-1}	1.05	0.95	0.9	0.8	0.7	0.65	0.45
	NS, residual F^-, mg L^{-1}	1	0.9	0.8	0.75	0.7	0.65	0.4
	%F^- removed	79	81	82	84	86	87	91
WBB	S, residual F^-, mg L^{-1}	1	0.9	0.8	0.76	0.7	0.6	0.45
	NS, residual F^-, mg L^{-1}	0.95	0.85	0.8	0.7	0.66	0.6	0.4
	%F^- removed	80	82	84	84.8	86	88	91
Shano	S, residual F^-, mg L^{-1}	1.5	1.4	1.3	1.2	1.1	0.98	0.9
	NS, residual F^-, mg L^{-1}	1.4	1.3	1.2	1.1	0.96	0.9	0.85
	%F^- removed	70	72	74	76	78	80.4	82
Debre Sina	S, residual F^-, mg L^{-1}	1.4	1.25	1.1	1.05	0.96	0.8	0.6
	NS, residual F^-, mg L^{-1}	1.3	1.2	1.1	1	0.9	0.8	0.58
	%F^- removed	72	75	78	79	80.8	84	88

Kara Kori	S, residual F^-, mg L^{-1}	1.2	1.1	1	0.9	0.8	0.7	0.5
	NS, residual F^-, mg L^{-1}	1.15	1.1	0.9	0.85	0.8	0.6	0.5
	%F^- removed	76	78	80	82	84	86	90
Dejen	S, residual F^-, mg L^{-1}	1.2	1.05	1	0.9	0.8	0.6	0.5
	NS, residual F^-, mg L^{-1}	1.1	1.05	0.96	0.85	0.78	0.64	0.46
	%F^- removed	76	79	80	82	84	88	90
Fiche	S, residual F^-, mg L^{-1}	1.28	1.1	0.88	0.79	0.72	0.68	0.48
	NS, residual F^-, mg L^{-1}	1.24	1.08	0.84	0.76	0.69	0.62	0.47
	%F^- removed	74.6	78.8	82.4	84.2	85.6	86.4	90.1
Chancho	S, residual F^-, mg L^{-1}	1.15	1.08	1	0.86	0.8	0.75	0.7
	NS, residual F^-, mg L^{-1}	1.1	1	0.91	0.82	0.76	0.75	0.68
	%F^- removed	77	78.4	80	82.8	84	85	86
Ambo	S, residual F^-, mg L^{-1}	1.25	1.06	0.96	0.85	0.78	0.67	0.41
	NS, residual F^-, mg L^{-1}	1.21	1.04	0.94	0.84	0.76	0.65	0.39
	%F^- removed	75	76.8	80.8	83	84.4	86.6	91.8
Holota	S, residual F^-, mg L^{-1}	1.08	0.68	0.58	0.53	0.47	0.4	0.26
	NS, residual F^-, mg L^{-1}	1.02	0.62	0.57	0.52	0.47	0.39	0.26
	%F^- removed	76.4	86.4	88.2	89.4	90.6	92	94.6
Wolisso	S, residual F^-, mg L^{-1}	1.2	1.15	1.1	1.05	1	0.96	0.78
	NS, residual F^-, mg L^{-1}	1.18	1.1	1.08	1.02	0.98	0.92	0.74
	%F^- removed	76	77	78	79	80	80.8	84.4
Wolikite	S, residual F^-, mg L^{-1}	0.69	0.51	0.44	0.39	0.3	0.21	0.15
	NS, residual F^-, mg L^{-1}	0.66	0.5	0.44	0.39	0.29	0.22	0.15
	%F^- removed	86.2	89.8	90.8	92.2	94	95.8	97
Hossana	S, residual F^-, mg L^{-1}	1.58	1.47	1.42	1.36	1.2	1	0.98
	NS, residual F^-, mg L^{-1}	1.54	1.45	1.4	1.34	1.15	0.96	0.94
	%F^- removed	68.4	70.6	71.6	72.8	76	80	80.4
Tullu Bollo	S, residual F^-, mg L^{-1}	1.48	1.42	1.36	1.28	1.1	0.98	0.76
	NS, residual F^-, mg L^{-1}	1.46	1.47	1.32	1.26	1	0.96	0.72
	%F^- removed	70.4	71.6	72.8	74.4	78	82	84.8
Butajira	S, residual F^-, mg L^{-1}	1.25	1.2	1.1	1.02	0.96	0.88	0.65
	NS, residual F^-, mg L^{-1}	1.23	1.18	1.05	1	0.92	0.86	0.62
	%F^- removed	75	76	78	79.6	80.8	82.4	87
Robe	S, residual F^-, mg L^{-1}	1.32	1.26	1.2	1.15	1	0.96	0.82
	NS, residual F^-, mg L^{-1}	1.3	1.24	1.2	1.12	0.98	0.92	0.8
	%F^- removed	73.6	74.8	76	77	80	80.8	83.6
Assella	S, residual F^-, mg L^{-1}	1.1	1.02	0.98	0.82	0.67	0.52	0.46
	NS, residual F^-, mg L^{-1}	1.04	1	0.96	0.78	0.63	0.5	0.43
	%F^- removed	78	79.6	80.4	83.6	86.6	89.6	90.8

Dodolla	S, residual F^-, mg L^{-1}	1.06	1	0.88	0.78	0.66	0.48	0.42
	NS, residual F^-, mg L^{-1}	1.02	0.96	0.82	0.76	0.62	0.44	0.4
	%F^- removed	78.8	80	82.4	84.4	87	90.4	91.6

Table 11. Effect of contact time on the fluoride removal with 50 g of 20 clay samples from 500 mL of 10.0 mg L^{-1} standard fluoride solution for both stirred and non-stirred solutions. (V :W =10 : 1; residual fluoride concentration in mg L^{-1})

Clay type	Contact of time, h	2	4	6	8	12	24	48
Fired	S, residual F^-, mg L^{-1}	3	2.8	2.6	2.4	2.2	2	1.8
	NS, residual F^-, mg L^{-1}	2.9	2.75	2.5	2.32	2.1	1.85	1.75
	%F^- removed	70	72	74	76	78	80	82
Gullalle	S, residual F^-, mg L^{-1}	1.75	1.62	1.52	1.47	1.21	0.95	0.88
	NS, residual F^-, mg L^{-1}	1.7	1.6	1.5	1.45	1.2	0.92	0.86
	%F^- removed	82.5	84.8	84.8	85.3	87.9	90.5	91.2
RBB	S, residual F^-, mg L^{-1}	1.6	1.5	1.4	1.3	1.2	0.9	0.7
	NS, residual F^-, mg L^{-1}	1.55	1.4	1.3	1.25	1.1	0.85	0.65
	%F^- removed	84	85	86	87	88	91	93
WBB	S, residual F^-, mg L^{-1}	1.9	1.8	1.6	1.4	1.3	1.1	0.9
	NS, residual F^-, mg L^{-1}	1.85	1.7	1.5	1.3	1.25	1	0.8
	%F^- removed	81	82	84	86	87	89	91
Shano	S, residual F^-, mg L^{-1}	2.2	1.9	1.7	1.6	1.5	1.25	0.8
	NS, residual F^-, mg L^{-1}	2.1	1.85	1.65	1.5	1.4	1.2	0.8
	%F^- removed	78	81	83	84	85	87.5	92
Debre Sina	S, residual F^-, mg L^{-1}	1.95	1.85	1.66	1.54	1.42	1.2	1.1
	NS, residual F^-, mg L^{-1}	1.9	1.8	1.62	1.52	1.38	1.12	1.05
	%F^- removed	80.5	81.5	83.4	84.6	85.8	88	89
Kara Kori	S, residual F^-, mg L^{-1}	1.8	1.6	1.4	1.3	1.1	0.95	0.6
	NS, residual F^-, mg L^{-1}	1.7	1.56	1.3	1.2	1.1	0.9	0.58
	%F^- removed	82	84	86	87	89	90.5	94
Dejen	S, residual F^-, mg L^{-1}	1.7	1.65	1.4	1.28	1.08	0.9	0.76
	NS, residual F^-, mg L^{-1}	1.65	1.5	1.38	1.25	1.05	0.85	0.75
	%F^- removed	83	83.5	86	87.2	89.2	91	92.4
Fiche	S, residual F^-, mg L^{-1}	1.68	1.55	1.45	1.38	1.26	1.14	1.1
	NS, residual F^-, mg L^{-1}	1.65	1.5	1.42	1.36	1.22	1.12	1
	%F^- removed	83.2	84.5	85.5	86.2	87.4	88.6	89

Chancho	S, residual F^-, mg L^{-1}	1.75	1.68	1.62	1.54	1.45	1.38	1.25
	NS, residual F^-, mg L^{-1}	1.72	1.64	1.6	1.5	1.42	1.36	1.2
	%F^- removed	82.5	83.6	83.8	84.6	85.5	86.2	87.5
Ambo	S, residual F^-, mg L^{-1}	1.64	1.5	1.4	1.22	1.1	0.98	0.59
	NS, residual F^-, mg L^{-1}	1.6	1.47	1.35	1.2	1.08	0.95	0.58
	%F^- removed	83.6	85	86	87.6	89	90.2	94.1
Holota	S, residual F^-, mg L^{-1}	1.5	0.9	0.82	0.73	0.67	0.56	0.34
	NS, residual F^-, mg L^{-1}	1.47	0.9	0.8	0.72	0.67	0.56	0.32
	%F^- removed	85	91	91.8	92.7	93.3	94.4	96.4
Wolisso	S, residual F^-, mg L^{-1}	1.89	1.86	1.78	1.62	1.6	1.25	1
	NS, residual F^-, mg L^{-1}	1.82	1.8	1.75	1.6	1.56	1.2	0.9
	%F^- removed	81	81.4	82.2	83.8	84	85	90
Wolikite	S, residual F^-, mg L^{-1}	0.9	0.75	0.54	0.45	0.38	0.3	0.19
	NS, residual F^-, mg L^{-1}	0.86	0.63	0.53	0.44	0.38	0.28	0.18
	%F^- removed	91	92.5	94.6	95.5	96.2	97	98.1
Hossana	S, residual F^-, mg L^{-1}	2.2	2.08	2	1.9	1.78	1.62	1.46
	NS, residual F^-, mg L^{-1}	2.15	2.04	1.9	1.85	1.72	1.6	1.42
	%F^- removed	78	79.2	80	81	82.2	83.8	85.4
Tullu Bollo	S, residual F^-, mg L^{-1}	2.1	1.98	1.94	1.88	1.76	1.58	1.4
	NS, residual F^-, mg L^{-1}	2	1.92	1.9	1.82	1.72	1.56	1.38
	%F^- removed	79	80.2	80.6	81.2	82.4	84.2	86
Butajira	S, residual F^-, mg L^{-1}	1.5	1.38	1.26	1.08	0.89	0.83	0.54
	NS, residual F^-, mg L^{-1}	1.48	1.35	1.22	1.02	0.88	0.8	0.53
	%F^- removed	85	86.2	87.4	89.4	91.1	91.7	94.6
Robe	S, residual F^-, mg L^{-1}	2	1.85	1.62	1.53	1.28	1	0.96
	NS, residual F^-, mg L^{-1}	1.8	1.7	1.55	1.48	1.2	0.95	0.9
	%F^- removed	80	81.5	83.8	84.7	87.2	90	90.4
Assella	S, residual F^-, mg L^{-1}	1.8	1.76	1.56	1.45	1.2	0.96	0.85
	NS, residual F^-, mg L^{-1}	1.75	1.72	1.5	1.42	1.1	0.92	0.8
	%F^- removed	82	82.4	84.6	85.5	88	90.4	91.5
Dodolla	S, residual F^-, mg L^{-1}	1.65	1.54	1.42	1.28	1.1	0.9	0.82
	NS, residual F^-, mg L^{-1}	1.6	1.52	1.4	1.25	1	0.88	0.8
	%F^- removed	83.5	84.6	86.8	87.2	89	91	92.2

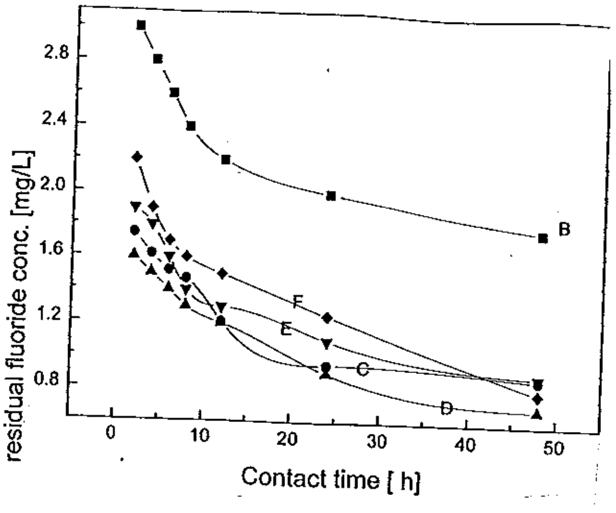


Figure 13. Residual fluoride concentration of 500 mL standard fluoride solution (10 mg F⁻/L) as a function of time of contact with 50 g fired (B), Gullalle (C), RBB (D), WBB (E), and Shano (F) clays.

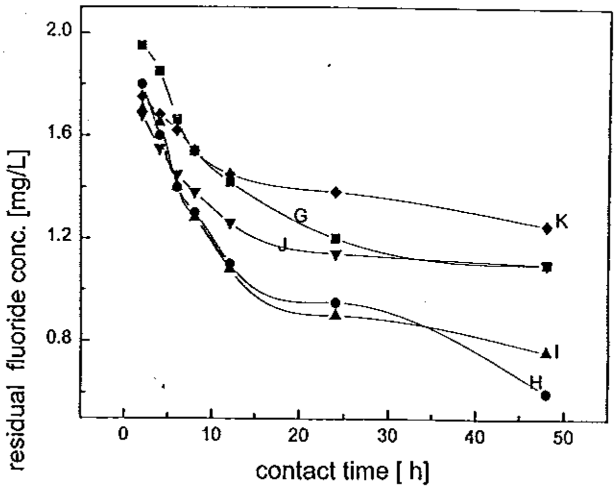


Figure 14. Residual fluoride concentration of 500 mL standard fluoride solution (10 mg F⁻/L) as a function of time of contact with 50 g of Debre Sina (G), Karakori (H), Dejen (I), Fiche (J), and Chancho (K) clays.

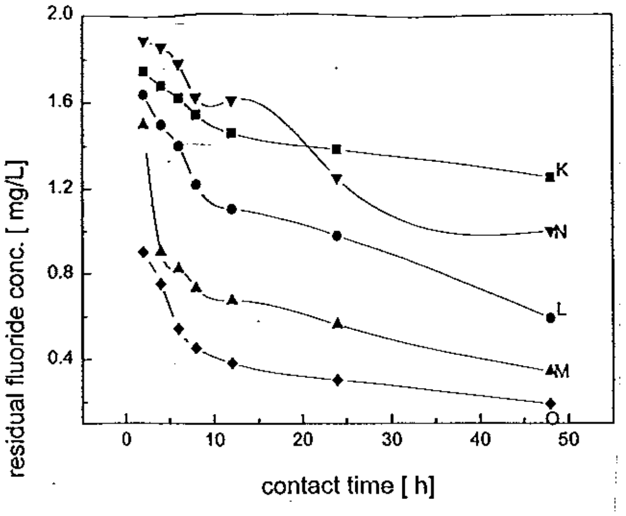


Figure 15. Residual fluoride concentration of 500 mL standard fluoride solution (10 mg F⁻/L) as a function of time of contact with 50 g of Ambo (L), Holota (M), Wolisso (N), Wolikite (O), and Hossan (P) clays.

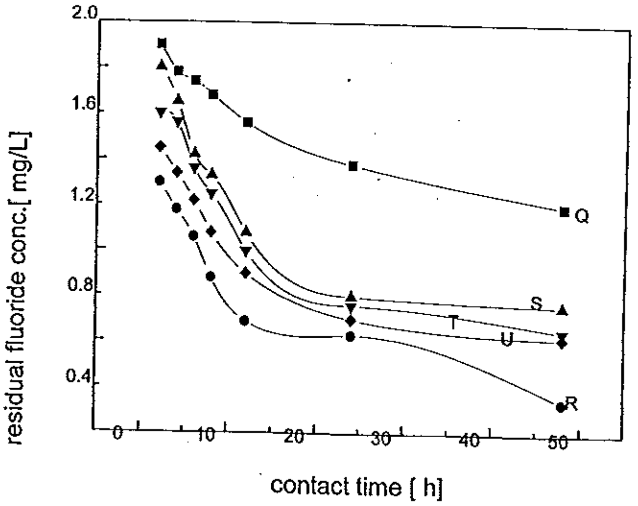


Figure 16. Residual fluoride concentration of 500 mL standard fluoride solution (10 mg F⁻/L) as a function of Time of contact with 50 g of Tullu Bollo (Q), Butajira (R), Robe (S), Assella (T), and Dodolla(U)clays.

Table 12. Effect of contact time on fluoride removal with 50 g of 6 clay samples from 500 mL of 12.8 mg L^{-1} Wonji Shoa ground water (pH = 8.2) for both stirred and non- stirred solutions (V : W = 10 : 1).

Clay type	Contact time, h	2	4	6	8	12	24	48
RBB	S, residual F$^-$, mg L^{-1}	1.38	1.15	0.84	0.65	0.54	0.41	0.14
	NS, residual F$^-$, mg L^{-1}	1.36	1.10	0.82	0.62	0.50	0.38	0.12
	%F$^-$ removed	88.5	90.0	93.0	94.6	95.5	96.6	99.0
Gullalle	S, residual F$^-$, mg L^{-1}	1.05	0.91	0.76	0.65	0.48	0.37	0.24
	NS, residual F$^-$, mg L^{-1}	1.05	0.87	0.74	0.62	0.46	0.35	0.20
	%F$^-$ removed	91.0	92.4	93.7	94.6	96.0	97.0	98.0
Ambo	S, residual F$^-$, mg L^{-1}	1.65	1.39	1.20	1.0	0.84	0.59	0.48
	NS, residual F$^-$, mg L^{-1}	1.62	1.36	1.15	0.97	0.80	0.58	0.46
	%F$^-$ removed	86.2	88.4	90.3	91.7	93.0	95.1	96.0
Holota	S, residual F$^-$, mg L^{-1}	1.50	1.26	1.20	0.96	0.80	0.52	0.40
	NS, residual F$^-$, mg L^{-1}	1.48	1.26	1.15	0.92	0.78	0.50	0.36
	%F$^-$ removed	88.3	90.2	90.6	92.8	93.75	96.0	96.9
Chancho	S, residual F$^-$, mg L^{-1}	1.70	1.54	1.49	1.26	1.0	0.95	0.78
	NS, residual F$^-$, mg L^{-1}	1.65	1.5	1.47	1.22	0.95	0.90	0.74
	%F$^-$ removed	85.8	87.2	87.6	89.5	91.6	92.0	93.5
Wolikite	S, residual F$^-$, mg L^{-1}	0.91	0.78	0.66	0.46	0.35	0.23	0.12
	NS, residual F$^-$, mg L^{-1}	0.90	0.68	0.56	0.40	0.32	0.20	0.10
	%F$^-$ removed	92.4	94.0	95.0	96.0	97.0	98.0	99.0

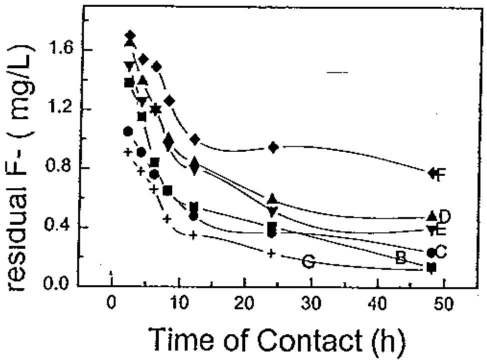


Figure 17. Residual fluoride concentration of 500 mL of 12.8 mg F$^-$/L Wonji Shoa ground water as a function of time of contact with 50 g of RBB (B), Gullalle (C), Ambo (D), Holota (E), Chancho (F), and Wolikite (G) clays.

9.4. Effect of pH

The result obtained (Table 13 and Figures 18-21) showed that the defluoridation efficiency is lower in the low and high pH range. The lower defluoridation efficiency in the low pH range is attributed to protonation of fluoride, i.e., the H^+ complexes a portion of fluoride ion, forming HF_2^- or HF ($HF + F^- = HF_2^-$), thus reducing the concentration of free fluoride available for adsorption. The lower defluoridation efficiency in the high pH range is accounted for interference from hydroxide ion, since both OH^- and F^- are isoelectronic and have the same charge, similar ionic radii (1.36 Å and 1.4 Å, respectively). The result obtained showed that an optimal defluoridation pH was 5-7 which encompass the pH of 5.0 and 10.0 mg L^{-1} standard fluoride solution. However, the pH of most natural water is in the range pH 8-9. Therefore, defluoridation efficiency of clays are lower for natural waters than the standard fluoride solution.

Table 13. Effect of pH on fluoride removal with 50 g of 20 clay samples from 500 mL of 10.0 mg L^{-1} standard fluoride solution at constant contact time of 1 h for both stirred and non-stirred solutions.

Clay type	pH of the solution	3	5	7	9
Fired	S, residual F^-, mg L^{-1}	3.5	2.7	2.9	3.45
	NS, residual F^-, mg L^{-1}	3.4	2.65	2.8	3.4
	%F^- removed	65.5	73	71	65
Gullalle	S, residual F^-, mg L^{-1}	3.1	2.1	2.7	3.2
	NS, residual F^-, mg L^{-1}	3	1.96	2.65	3.16
	%F^- removed	69	79	73	68
RBB	S, residual F^-, mg L^{-1}	25	1.5	1.8	2.9
	NS, residual F^-, mg L^{-1}	2.4	1.4	1.7	2.8
	%F^- removed	75	85	82	71
WBB	S, residual F^-, mg L^{-1}	3.3	2.5	3	3.85
	NS, residual F^-, mg L^{-1}	3.24	2.26	2.9	3.6
	%F^- removed	67	75	70	61.5
Shano	S, residual F^-, mg L^{-1}	3.2	2.5	3	3.4
	NS, residual F^-, mg L^{-1}	3.2	2.4	2.9	3.3
	%F^- removed	68	75	70	66

Debre Sina	S, residual F^-, mg L^{-1}	2.7	1.65	2.3	3
	NS, residual F^-, mg L^{-1}	2.64	1.54	2.3	3
	%F^- removed	73	83.5	77	70
Kara Kori	S, residual F^-, mg L^{-1}	3.6	2.8	3.1	3.9
	NS, residual F^-, mg L^{-1}	3.5	2.7	3	3.8
	%F^- removed	64	72	69	61
Dejen	S, residual F^-, mg L^{-1}	2.9	2.1	2.64	3
	NS, residual F^-, mg L^{-1}	2.64	2.0	2.52	2.96
	%F^- removed	71	89	73.6	70
Fiche	S, residual F^-, mg L^{-1}	3	2.3	2.75	3.25
	NS, residual F^-, mg L^{-1}	2.9	2.2	2.65	3.2
	%F^- removed	70	77	72.5	67.5
Chancho	S, residual F^-, mg L^{-1}	2.31	1.65	2.1	2.51
	NS, residual F^-, mg L^{-1}	2.21	1.6	2	2.45
	%F^- removed	77	83.5	79	74.9
Ambo	S, residual F^-, mg L^{-1}	2.52	1.5	2.1	2.8
	NS, residual F^-, mg L^{-1}	2.42	1.4	2	2.7
	%F^- removed	74.8	85	89	82
Holota	S, residual F^-, mg L^{-1}	2.3	1.4	1.9	2.52
	NS, residual F^-, mg L^{-1}	2.22	1.3	1.88	0.45
	%F^- removed	77	86	81	74.8
Wolisso	S, residual F^-, mg L^{-1}	3.4	2.3	2.6	3.6
	NS, residual F^-, mg L^{-1}	3.3	2.3	2.55	3.45
	%F^- removed	66	77	74	64
Wolikite	S, residual F^-, mg L^{-1}	2.4	1.3	1.5	3
	NS, residual F^-, mg L^{-1}	2.35	1.28	1.46	2.9
	%F^- removed	76	87	85	70
Hossana	S, residual F^-, mg L^{-1}	3.4	2.6	2.8	3.7
	NS, residual F^-, mg L^{-1}	3.3	2.5	2.75	3.65
	%F^- removed	66	74	72	63
Tullu Bollo	S, residual F^-, mg L^{-1}	3.2	2.3	2.8	3.3
	NS, residual F^-, mg L^{-1}	2.5	2.1	2.75	3.25
	%F^- removed	66.8	77	72	67
Butajira	S, residual F^-, mg L^{-1}	3	1.7	2.3	3.24
	NS, residual F^-, mg L^{-1}	2.9	1.6	2.25	3.16
	%F^- removed	70	83	77	67.6
Robe	S, residual F^-, mg L^{-1}	2.74	1.64	2.13	3
	NS, residual F^-, mg L^{-1}	3.66	1.6	2.1	2.9
	%F^- removed	72	83.6	78.7	70

Assella	S, residual F^-, mg L^{-1}	2.58	1.83	2.42	3
	NS, residual F^-, mg L^{-1}	2.52	1.8	2.3	2.9
	%F^- removed	74.2	81.7	75.8	70
Dodolla	S, residual F^-, mg L^{-1}	2.56	1.8	2.4	2.92
	NS, residual F^-, mg L^{-1}	2.53	1.75	2.25	2.88
	%F^- removed	74.4	82	76	71.8

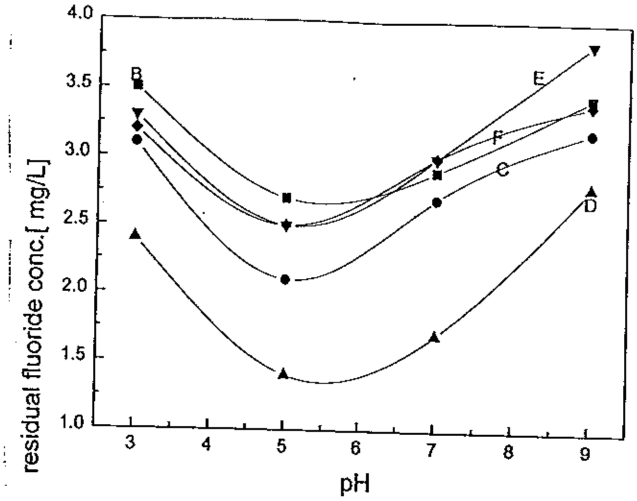


Figure 18. Residual fluoride concentration as a function of pH of 500 mL of standard fluoride solution (10 mg F^-/L) of Fired (B), Gullalle (C), RBB (D), WBB (E), and Shano (F) clays.

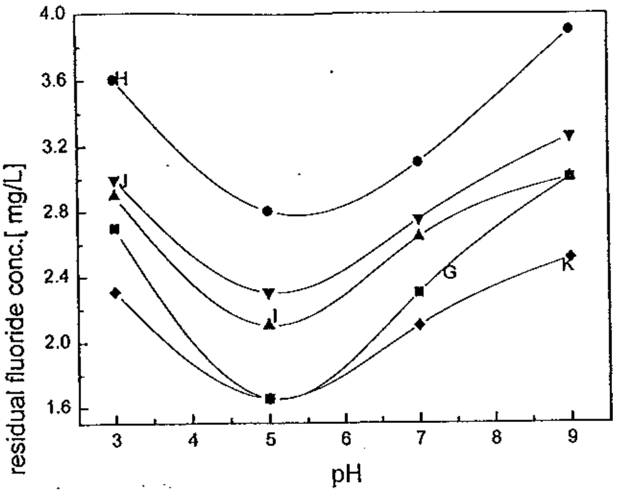


Figure 19. Residual fluoride concentration as a function of pH of 500 mL of standard fluoride solution (10 mg F^-/L) for Debre Sina [G], Karakori [H], Dejen [I], Fiche [J], and Chancho [K] clays.

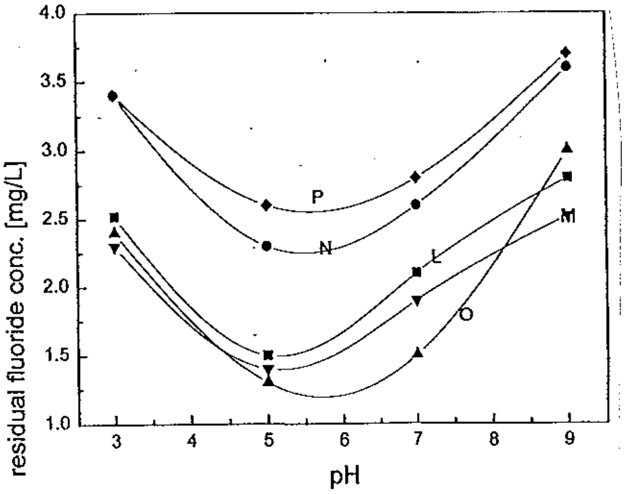


Figure 20. Residual fluoride concentration as a function of pH of 500 mL of standard fluoride solution (10 mg F^-/L) for Ambo [L], Holota [M], Wolisso [N], Wolikite [O], and Hossana [P] clays.

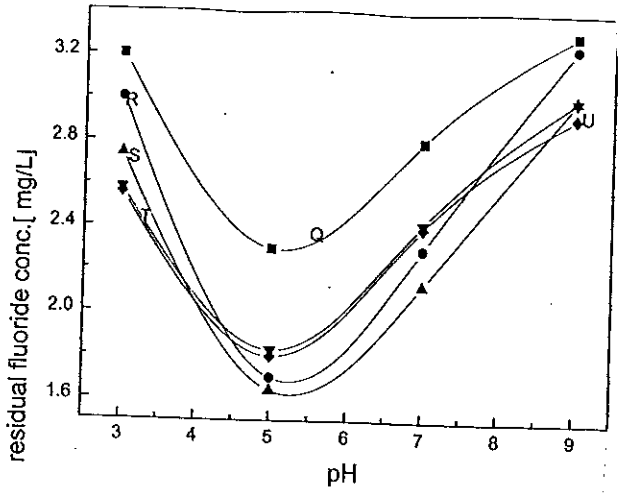


Figure 21. Residual fluoride concentration as a function of pH of 500 mL of standard fluoride solution (10 mg F^-/L) for Tullu Bollo [Q] , Butajira [R], Robe [S], Assella [T] , and Dodolla [U] clays.

9.5. Defluoridation Capacity of Clay Samples

Defluoridation capacity of 50 g of 20 clay samples on 500 mL of 10.0 mg L^{-1} standard fluoride solution at constant contact time of 1 h was calculated and given in Table 14. The defluoridation capacity order of the clays are therefore, Wolikite clay > Chancho clay > RBB clay > Holota clay > Dodolla clay > Fiche clay > Ambo clay > Dejen clay > WBB clay = Wolisso clay > Gullalle clay > Debre Sina clay = Butajira clay > Hossana clay > Assella clay > Robe clay = Kara Kori clay > Shano clay = Tullu Bollo > fired clay. Among the clays studied, therefore, Wolikite clay was found to be the most efficient, but fired clay was found to be the least efficient of the defluoridation.This might have been due to geochemical effect in the former case and due to temperature effect in the latter case.

Table 14. Defluoridation capacity of 50 g of clay samples on 500 mL of 10.0 mg L^{-1} standard fluoride solution at constant contact time of 1 h

Type of clay	Defluoridation capacity (mg F^{-1}/Kg)	Type of clay	Defluoridation capacity (mg F^{-1}/Kg)
Fired	138.0	Ambo	163.0
Gullalle	158.0	Holota	168.0
RBB	170.0	Wolisso	160.0
WBB	160.0	Wolikite	178.0
Shano	150.0	Hossana	154.0
Debre Sina	156.0	Tullo Bollo	150.0
Kara Kori(Wollo)	152.0	Butajira	156.0
Dejen	162.0	Robe (Arsi)	152.0
Fiche	164.0	Assella	153.0
Chancho	172.0	Dodolla	167.0

9.6. Defluoridation Capacity of Clay Samples on Wonji Shoa Ground Water

Defluoridation capacity of 50 g of 6 clay samples on 500 mL of Wonji Shoa ground water (12.8 mg F^{-} L^{-1}) at constant contact time of 1 h was calculated and is given in Table 15. These clay samples were selected due to their efficient defluoridation capacity. Among the clay studied Wolikite clay was found to be the most efficient, but Chancho clay was found to be the least. Wolikite clay presumably has larger active sites or binding surfaces than Chancho clay.

Table 15. Defluoridation capacity of 50 g of 6 clay samples on 500 mL of Wonji Shoa ground water (12.8 mg F^{-} L^{-1}) at constant contact time of 1 h

Type of clay	Defluoridation capacity (mg F^{-1} /Kg)
RBB	220.0
Gullalle	210.0
Ambo	213.0
Holota	218.0
Chancho	205.0
Wolikite	230.0

9.7. Regeneratin/Desorption Experiment

This experimental finding suggested that it is possible to regenerate/desorp the fluoride-clay complex using sodium hydroxide solution and the regenerated clay can be reused for defluoridation. The results obtained in Figures 14-16 showed that 50 g of regenerated Wolikite clay reduced 10 mg L^{-1} standard fluoride solution down to approximately 2 mg L^{-1} at constant contact time of 1 h. The percentage of fluoride removal capacity was calculated to be 80 %. This experimental result indicates that the clays can be regenerated and reused for defluoridation at household and community scales.

Table 16. Effect of mass of regenerated Wolikite clay on 10 mg L^{-1} standard fluoride solution

mass of clay, g	10	20	30	40	50
S, residual F^-, mg/L	2.7	2.54	2.38	2.2	1.9
NS, residual F^-, mg/L	2.68	2.5	2.36	2.1	1.85
%F^- removed	73.0	74.6	76.2	78.0	81.0

Table 17. Effect of volume of 10 mg L^{-1} standard fluoride solution on regenerated Wolikite clay

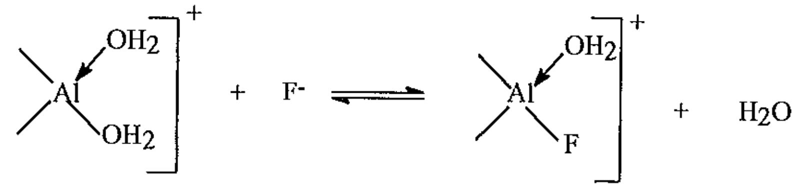
Volume of solution, mL	100	200	300	400	500
S, residual F^-, mg/L	1.60	1.75	2.00	2.10	2.2
NS, residual F^-, mg/L	1.50	1.70	1.95	1.98	2.10
%F^- removed	84.0	82.5	80.0	79.0	78.0

Table 18. Effect of time on regenerated Wolikite clay

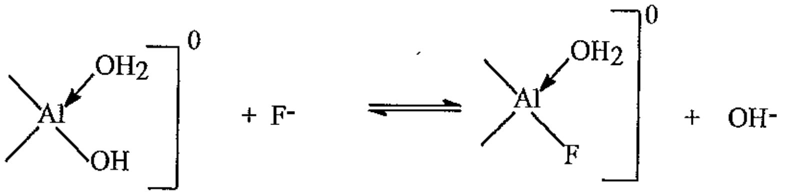
contact time, h	2	4	6	8	12	24	48
S, residual F^-, mg/L	1.40	1.20	1.10	0.98	0.86	0.78	0.60
NS, residual F^-, mg/L	1.35	1.10	1.0	0.95	0.82	0.75	0.58
%F^- removed	86.0	88.0	89.0	90.2	91.4	92.2	94.0

9.8. Proposed Mechanism

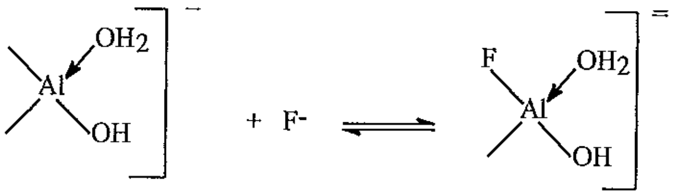
Stoichiometric release of OH^- from clay by fluoride has been reported by Dickman and Bray, [51-52] who concluded that fluoride replaces the hydroxide ion found in the clay. Many researchers [34, 43, 51-52] have found that anion adsorption/ion-exchange on clay minerals are aquo groups ($-M-OH_2^+$) and hydroxo groups (-M-OH). Therefore, adsorption/ion-exchange of fluoride by clay minerals may involve either of the following equilibria depending up on the surface of stereochemistry of the clay minerals.



(i)



(ii)



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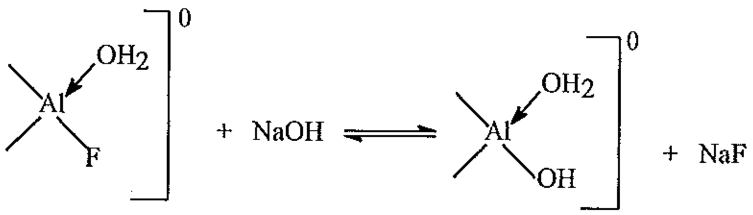

(iv)

Further, the partial desorption of fluoride from 1% (w/v) NaOH solution is explained due to OH^- = F^- exchange phenomena and it further suggests the possible occurrence of fluoride-clay complex that can not be easily desorped as shown in mechanism (iv).

This was confirmed by measuring the pH of the solution after it had been loaded with clay soils for time effect of Wolikite clay soil.

Example of change of pH of Wolikite clay soil for 10.0 mg L^{-1} standard fluoride solution.

Time, h	2	4	6	8	12	24	48
pH	7.2	7.4	7.6	7.8	8.0	8.10	8.4

By mixing water and clay, the color of mixture of clays and fluoride solution turned brownish or grayish depending on the color of the clay used for defluoridation. The turbidity of the mixture was higher at the beginning, however, gradually reduced as the clay particles get sedimented. Stirring retarded sedimentation.

After nearly 24 h the particles get sedimented and the solution became very clear. No major hydrochemical changes (apart from reduction in fluoride concentration) seemed to take place in the mixture during the defluoridation process. The chemical reactions take place are not known in detail, but adsorption/ion-exchange is most likely to play pivotal role.

The defluoridating efficiency of fired clay chips is very poor among the used clays. All the clay soils used have been seen to reduce fluoride concentration from standard fluoride solution, however, more quickly in the stirring conditions due to the homogeneity of the solution. There is no significant difference between stirring and non-stirring samples in the reduction of fluoride concentration. The laboratory studies on the used clay samples indicate that clay soils may be used to improve the quality of high fluoride drinking water at national, community and household levels.

10. CONCLUSION

The immersion of clay soil into standard fluoride solution caused a decrease in the fluoride concentration in all samples. In most cases a relatively sharp decrease in the fluoride concentration was observed for all controlling factors. It is to be emphasized that there is a great tendency in the fluoride binding capacity of high land soils. The altitude is most likely irrelevant; the crucial point might seem to be whether precipitation and surface waters have depleted or enriched the soil as to fluoride. The best defluoridating agent was found to be unfired black and red soils, however, there was no systematic difference between black and red clay soils in fluoride binding capacity. Hence, black and red clay soils from the Ethiopian high land may be used for inexpensive and effective removal of excessive fluoride in the drinking water.

The fired clay chips was the least among the defluoridating media used. This accounts for the effect of firing temperature which greatly influence the fluoride binding capacity of the clay soil. The firing sterilizes the soil, and reduces the inherent tendency of soiling of water. Moreover, firing requires energy, and may thereby increase local deforestation and so not recommended to use fired clay chips. It is evident that the fluoride binding process is enhanced by stirring the NaF solution. However, stirring does nothing to do with increasing the total fluoride binding capacity of the clay soils.

Based on the defluoridation capacity of clay soils it may be concluded that 1 Kg clay soil is sufficient to absorb approximately 200 mg F^{-1}. Accordingly, 1 Kg clay soil may reduce the fluoride content of 20 L of water from 10.0 mg L^{-1} to 1.5 mg L^{-1}. Twenty litre water would seem to be sufficient to meet the need for drinking and cooking in a low sized family.

Therefore, fluoride depleted topsoil may be able to reabsorb fluoride, and thereby remove excessive fluoride from high fluoride ground waters.

The result of this study, make it possible to outline preliminary guidelines regarding the defluoridation of waters at community and village levels.

Excessive fluoride in waters can be efficiently removed by the use of natural clay in the Ethiopia high lands. The pH of 5-6 may be maintained to maximize the defluoridation. A 12.8 mg L^{-1} fluoride containing natural water has been brought down to the values of the maximum permissible level of 1.5 mg L^{-1} fluoride by simply mixing with clay.

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