

JIMMA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY



A THESIS ON:

**REMOVAL OF FLUORIDE FROM AQUEOUS SOLUTION USING FIRED
CLAY SOIL PILLARED WITH TEA LEAF ASH COMPONENTS**

November, 2013

Jimma, Ethiopia

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**A THESIS SUBMITTED TO SCHOOL OF GRADUATE STUDIES JIMMA
UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTERS OF SCIENCE IN CHEMISTRY (ANALYTICAL CHEMISTRY
STREAM).**

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Removal of fluoride from aqueous solution using fired clay soil pillared with tea leaf ash components

By

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A Thesis Submitted to School of Graduate Studies Jimma University in Partial Fulfillment of the Requirements for the Degree of Masters of Science in Chemistry (Analytical Chemistry stream)

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Acknowledgements

First of all my heartfelt gratitude goes to my advisor *Dr. Dejene Ayele* for his valuable scientific comments and guidance start from the beginning to the end.

I gratefully acknowledge Department of Chemistry, Jimma University for its unreserved help and encouraging me by providing necessary materials. I would also like to express my gratitude to JUCAVM, Department of Post Harvest Management for their material support. I am also very thankful for Mr. Bayu Dume for his help in this work.

Last but not the least I wish to thank my family and friends for their moral support, consistent encouragement and valuable advice

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Abbreviations and Acronyms

FC

Fired clay soil

FC-TLA

Fired clay soil pillared with tea leave ash

WHO

World Health Organization

Abstract

This study reports on the adsorption of fluoride ion from aqueous solutions by using fired clay soil, pillared with tea leave ash components. The potential of low cost material fired clay soil and fired clay soil pillared with tea leave ash components for fluoride removal from aqueous solution was evaluated by using fluoride ion selective electrode. Pillaring of clay soil with tea leave ash was done by thoroughly mixing fifteen gram of tea leave ash and three hundred gram of clay soil using distilled water and it was aged for 96 hours until it was dried. Untreated clay soil and clay soil pillared with tea leave ash components were fired in an electrical furnace at 570 °C for 3 hrs. Batch adsorption experiments were carried out and the effects of pH, contact time, initial adsorbate concentration, adsorbent dose and temperature of the solution were investigated. Adsorption of fluoride by fired clay soil and fired clay soil pillared with tea leave ash was observed to sharply increase from pH 4 to 7 then decreased. The adsorption of fluoride was observed to increase with initial concentration. The fluoride adsorption process was better represented by the Freundlich isotherm model than Langmuir, with correlation coefficient (r^2) of 0.930 and 0.998 for fired clay soil and fired clay soil pillared with tea leave ash components respectively. The maximum adsorption efficiencies obtained were 75% for fired clay soil and 90% for fired clay soil pillared with tea leave ash components at pH 7 for both adsorbents. The Kinetic of fluoride adsorption followed the pseudo-second-order kinetic model as determined by stronger correlation (r^2 0.946 and 0.991) for fired clay soil and fired clay soil pillared with tea leave ash components respectively and higher agreement between q_e and q_{exp} . The maximum adsorption capacity obtained was 0.913 mg/g for fired clay soil and 2.746 mg/g for fired clay soil pillared with tea leave ash components. It can be concluded that fired clay soil pillared with tea leave ash is a good and cheap adsorbent with high potential for the adsorption and removal of fluoride from fluoride contaminated water and could therefore serve as effective and efficient adsorbent for treatment of drinking waters in terms of high adsorption capacity.

Key words: Defluoridation, pillared clay soil, batch adsorption, isotherm study, defluoridation efficiency.

1) Introduction

Management of contaminants such as fluoride is a major public issue. Fluoride enrichment in natural water can occur either by geological processes or from industries [1]. Fluoride of geogenic origin in groundwater which is used as a source of drinking water is a major concern because fluoride content above permissible levels is responsible for human dental and skeletal fluorosis. Consequently, water sources containing elevated levels of fluoride have to be treated.

Fluorine in its elemental form is a greenish, highly reactive, diatomic gas. It is the most electronegative of all known elements and rarely occurs free in nature. It generally combines with other elements to form fluorides and is normally found as the fluoride ion (F^-) in minerals [2]. Fluoride is found in both surface waters and ground water because some fluoride compounds present in the earth's upper crust are readily soluble in water. The average earth's crust abundance is 300 mg kg^{-1} spread in a wide variety of minerals such as fluorspar, rock phosphate, cryolite, apatite, mica, hornblende, and others [3]. The most common fluoride mineral is fluorite (CaF_2), a compound with low solubility that can be present in igneous and sedimentary rocks [4]. The concentration of fluoride in water is normally controlled by the fluorite solubility.

In streaming surface freshwater, fluoride concentrations are usually lower than in groundwater because of the shorter contact time between water and rock. The natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, the temperature and the action of other chemical elements [5]. The fluoride load in the aquatic environment due to industrial discharge is at least 100- fold higher compared to that which arises due to leaching of fluoride bearing minerals [6]. Fluoride, as a dissolved constituent of drinking water, is perhaps the only substance producing divergent health effects on the consumer depending upon its relative proportions. The toxicity of fluoride is influenced by high ambient temperature, alkalinity, calcium and magnesium contents in the drinking water. The drinking water standard for fluoride set by WHO is 1.5 mg/L [7].

Fluoride concentration higher than 1.5 mg/L is reported to be harmful to the teeth and bone structure of men and animals [8]. Based on the nature of processes, the defluoridation techniques

that have been employed so far are adsorption, ion exchange, precipitation, electrochemical and membrane techniques. However these techniques are not widely used primarily because of their high cost, inefficiency or failure in mass scale application. Therefore, the search for a suitable low cost and environmental friendly method for the efficient removal of fluoride in drinking water is crucial. In this work fired clay soil pillared with tea leave ash components was attempted.

Studies on the adsorptive removal of fluoride by using fired clay soil are reported in the literature [9]. However, there is no reported study on the removal of fluoride by fired clay soil pillared with tea leave ash. Thus, the objectives of this study are to investigate the capacity of fired clay soil (FC) and fired clay soil pillared with tea leave ash (FC-TLA) for the removal of fluoride. Tea leaf ash was chosen for pillaring due to its high content of metallic elements [10] which can increase the positive character of the clay soil and may increase the fluoride removal capacity of the fired clay soil.

1.1 Statement of the problem

Access to potable water is one of the main problems in Ethiopia especially in rift valley areas. These areas are highly affected by high concentration of fluoride in water. Even though fluoride is essential element for human at low concentrations, it has negative effect when it is higher than the permissible concentration. Therefore this element should be removed from drinking water when it is found to be higher than the permissible concentration.

A number of methods have been developed for the removal of this toxic element from drinking water. However, most of the methods are either costly and not affordable by developing countries or culturally unacceptable by societies. Therefore, this study was aimed to develop an economically sound and efficient method of removing fluoride from drinking water by using clay soil and tea leave waste.

1.2 Objective of the study

1.2.1 General Objective

To develop method for removal of fluoride from drinking water by using fired clay soil pillared with tea leaves ash components.

1.2.2 Specific Objectives

- ✓ To prepare tea leaf ash pillared clay soil
- ✓ To optimize fluoride adsorption parameters
- ✓ To study fluoride removal efficiencies of pillared clay soils
- ✓ To identify the adsorption mechanisms of fluoride onto FC and FC-TLA in terms of kinetics and isotherms.

1.3 Significance of the study

Successful outcome of this research project would be beneficial to millions of people in Ethiopia and many other parts of the world who are suffering from excess fluoride in their drinking waters.

2) Literature Review

2.1 Fluoride

Fluoride is a naturally occurring compound derived from fluorine, the 13th most abundant element on Earth. It is found in rocks, soil, and fresh and ocean water. Fluoride is present naturally in almost all foods and beverages including water, but levels can vary widely. It is added to drinking water to provide public protection from dental caries. It is beneficial especially to young children below eight years of age when present within permissible limits of 1.0 – 1.5 mg L⁻¹ F⁻ for calcification of dental enamel.

2.1.1 Occurrence in natural water

Fluoride occurs naturally in public water systems as a result of runoff from weathering of fluoride-containing rocks and soils and leaching from soil into groundwater. Atmospheric deposition of fluoride-containing emissions from coal-fired power plants and other industrial sources also contributes to amounts found in water, either by direct deposition or by deposition to soil and subsequent runoff into water [11].

2.1.2 Health effect

Fluorides in drinking water may be beneficial or detrimental depending on its concentration and total amount ingested. Fluoride is beneficial especially to young children below eight years of age when present within permissible limits of 1.0 – 1.5 mg L⁻¹ F⁻ for calcification of dental enamel. Excess fluorides in drinking water cause dental fluorosis and/or skeletal fluorosis [12]. Research of several investigators during the last 5-6 years has proven that lifelong impact and accumulation of fluorides causes not only human skeletal and teeth damage, but also changes in the DNA-structure, paralysis of volition, cancer, etc [13]. Ethiopia is one of the 23 countries where the population suffers from the consumption of fluoride rich drinking water [14]. People in several areas of the Ethiopian Rift Valley are consuming water with up to 33 mg/L of fluoride [15]. Endemic fluorosis caused by fluoride in the environment is a global geochemical disease.

2.2 Defluoridation Methods:

Defluoridation is process of removal of fluoride ion in drinking water. All the defluoridation method may broadly be classified in two categories namely i) Additive methods and ii) Adsorptive methods. In additive methods, certain reagents are added and optimum conditions for the defluoridation are maintained. A fluoride ion present in water react with the reagents added and forms an insoluble complex and is removed as flocs. In adsorptive methods, a bed of greater surface activity is chosen and water is passed through the bed. Due to surface activity, the fluoride ion gets preferentially adsorbed on the bed surface thereby causing a reduction of fluoride ion in the exit stream [16].

The different method so far tried for the removal of excess fluoride from water can be broadly classified in four categories namely.

- Adsorption method
- Ion Exchange method
- Precipitation method
- Miscellaneous methods [17].

2.2.1 Adsorption Methods:

2.2.1.1 Activated Carbon:

It can be prepared from the different raw materials, such as wood, lignite, coal, bone, petroleum residues, nutshells and also from other low cost/waste materials like the rice-husk, saw dust, coconut shell, tree bark, cotton waste etc. by subjecting them to a high temperature heating with or without chemical treatment. The removal of fluoride by coconut pith carbon (CPC) was studied [18]. The activated carbon prepared by carbonization of CPC in presence of sulphuric acid was used for defluoridation without any chemical treatment as well as after impregnation with different alum dose.

2.2.1.2 Clays as sorbents for fluoride

The term clay is often used in a non-specific way and could refer to: (a) soil consisting of a range of small particle sizes (eg. particle size $< 1/256$ mm on the Udden-Wentworth scale), (b) very fine-grained earthy substances comprising a combination of minerals, inorganic amorphous material and organic matter or (c) a specific clay mineral. The clay minerals are minerals in the phyllosilicate mineral group and as the name implies (Greek: *pyllon*, leaf), most of these minerals have a platy habit. In this study the term clay refers to naturally occurring, very fine-grained earthy material composed primarily of clay minerals. Clays are potentially good adsorber of anions since they contain crystalline minerals such as kaolinite, smectite and amorphous minerals such as allophane and other metal oxides and hydroxides which could adsorb anions such as F^- . Finally, the rock type laterite which represents a group of deposits consisting of residual insoluble ferric and aluminium oxides, clay minerals and quartz, formed by weathering of rocks is also a potential adsorber of anions [19].

The structure of the clay plays a very important role in determining the charge on the clay surface and type of exchange that can occur with ions in solution. In general the more negative the surface the better the sorption will be for positively charged metal ions. The pH parameter plays a dominant role in determining the adsorption capacity as pH modifies the charges on edge positions in phyllo silicates and also those of variably charged minerals such as gibbsite, hematite and goethite. Charges are generally positive under acid conditions and negative in an alkaline environment. The specific pH range for positive and negative surface charge will of course be a function of the pKa values of the metal hydroxides present. An acid pH will favor adsorption of negatively charge ions while alkaline conditions will enhance adsorption of positive ions.

Many studies report on the fluoride adsorption capacities of clays and soils and their potential use as sorbents. The first comprehensive study of fluoride adsorption onto minerals and soils was published in 1967 [20]. The results showed that excess fluoride in water could be removed to different degrees by adsorption onto a variety of soil and mineral types, in particular aluminium

hydroxides. It was found that the adsorption is concentration-dependent and can be described by a Langmuir isotherm. Adsorption is typically followed by the release of OH^- ions.

2.3 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution [21].

2.3.1 Adsorption process

Adsorption arises as a result of the unsaturated and unbalanced molecular forces that are present on every solid surface. Thus, when a solid surface is brought into contact with a liquid or gas, there is an interaction between the fields of forces of the surface and that of the liquid or gas. The solid surface tends to satisfy these residual forces by attracting and retaining on its surface the molecules, atom, or ion of the gas or liquid. This result in a greater concentration of the gas or liquid in the near vicinity of solid surface than in the bulk gas or vapour phase, despite the nature of gas or vapour. The process by which this surface excess is caused is called adsorption.

The adsorption involves two types of forces as physisorption (characteristic of weak Van der Waals forces) or chemisorptions (characteristic of covalent bonding).

- a. **Physical adsorption:** The adsorbate is bound to the surface by relatively weak Van der Waals forces, which are similar to the molecular force of cohesion and are involved in the condensation of vapors into liquids.
- b. **Chemical adsorption:** Chemisorptions involves exchange or sharing of electrons between the adsorbate molecules and the surface of the adsorbent resulting in a chemical reaction. The bond formed between the adsorbate and the adsorbent is essentially a chemical bond and is thus much stronger than in the physisorption [22].

2.4 Adsorption Kinetic studies

Adsorption is a time-dependent process and it is very important to know the rate of adsorption for design and evaluate the adsorbent in removing the fluoride in wastewater. In many cases, the kinetics of adsorption based on the overall adsorption rate by the adsorbents is described by the first order Lagergren model and pseudo second-order.

The pseudo first-order rate expression of Lagergren is given as:

$$\frac{dq}{dt} = k_1(q_e - q_t) \dots \dots \dots (1) \quad [23]$$

Where q_e and q_t are the amount of fluoride ion adsorbed on adsorbent at equilibrium and time t , respectively (mg/g), and k_1 is the rate constant of the first order adsorption (min^{-1}). Integrating equation (1) for the boundary conditions $t = 0$ to $t = t$ is the following:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \dots \dots \dots (2)$$

The plot of $\log(q_e - q_t)$ versus t will give a straight line and the value of k_1 can be obtained from the slope of the graph.

The second-order kinetic model is expressed as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \dots \dots \dots (3)$$

Where, k_2 is the pseudo-second-order rate constant of adsorption ($\text{g mg}^{-1}\text{min}^{-1}$). The linearised integrated form of (3) is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \dots \dots \dots (4)$$

If the pseudo second-order kinetics is applicable to the system, then the plot of $\frac{1}{q_t}$ versus t of

Equation 4 will give a linear relationship with $\frac{1}{q_e}$ and $\frac{1}{k_2 q_e^2}$ as a slope and intercept, respectively.

The values of q_e and k_2 can be determined from the slope and intercept and there is no need to know any parameters beforehand. The pseudo second-order kinetics model has been successfully applied to several adsorption systems as reported by [24, 25]

2.5 Adsorption isotherms

There are several isotherm equations available for analyzing experimental adsorption equilibrium parameters, the most common being used are the Langmuir and Freundlich models. The Langmuir isotherm model is based on the assumption that there are a finite number of active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between adsorbed molecules. A well known linear form of the Langmuir equation can be expressed as

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_L} \dots \dots \dots (5) \quad [26]$$

Where q_e is the amount of fluoride ion adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), and q_m and b_L are Langmuir constants related to the maximum adsorption capacity (mg/g) and energy of adsorption (L/mg).

According to Equation 5, when the adsorption obeys the Langmuir equation, a plot of C_e / q_e versus C_e should be a straight line with a slope of $1/q_m$ and intercept $\frac{1}{q_m b_L}$ [27]. This important characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless factor, R_L which is defined as:

$$R_L = \frac{1}{1 + b_L C_o} \dots \dots \dots (6) \quad [28]$$

The R_L values indicate the type of adsorption as either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

The Freundlich isotherm model applies to adsorption on heterogeneous surfaces with interaction between the adsorbed molecules, and is not restricted to the formation of a monolayer. This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and, correspondingly, the sorption energy exponentially decreases on completion of the sorption centers of the adsorbent. The well-known expression for the Freundlich model is given as:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \dots \dots \dots (7) \quad [28]$$

Where q_e is the amount adsorbed at equilibrium (mg/g), K_f is the Freundlich constant, $1/n$ is the heterogeneity factor which is related to the capacity and intensity of the adsorption, and C_e is the equilibrium concentration (mg/L). The values of K_f and $1/n$ can be obtained from the slope and intercept of the plot of $\log q_e$ against $\log C_e$. Value of $1/n$ ranges from 0 to 1 and the closer this value to zero, the more heterogeneous the adsorbent surface.

3. Materials and Methods

3.1 Sample collection

Clay soil sample was collected from the outskirts of Jimma town and tea leave was collected from Gumaro Tea Development farm which is 293 km from Jimma.

3.2 Calibration of the Ion Selective Electrode

The sensor was connected to pH meter and placed in mV mode. 100 mL of deionized water was placed in to beaker with stir bar. Then the electrode was placed into prepared sample. 1 mL of 0.1 M F⁻ standard was added to beaker. Potential (mV) value was recorded when it became stable. An additional of 10 mL of the standard was added to the solution. Then potential (mV) was recorded. This value was more negative than the previous value. The difference in potential between these two mV values was -54 mV which is acceptable value according to the manual of the manufacturer of the electrode. These procedures were done before determination of fluoride ion for each parameter.

3.3 Reagents and Solutions

All chemicals used in this study were used without any purification. Deionised water was used for the preparation of stock standard solution of fluoride and also for all subsequent dilutions. A stock solution of fluoride (100 mg/L) was prepared by dissolving 221 mg NaF (BDH, England) in 1000 mL deionized water. Working solutions of the desired concentrations were prepared by serial dilution of the stock solution. Hydrochloric acid (Reideal Dehaen, 37%) and/or sodium hydroxide (Fischer scientific United Kingdom) solutions (0.1 M) were used throughout the experiments to adjust the pH of solutions. Glacial acetic (Riedel-de Haën, Germany) sodium acetate (Riedel-de Haën, Germany), Potassium hydrogen phosphate (Finkem, India), Potassium dihydrogen phosphate (Finkem, India) conc.NH₃, (Mumbai, India), ammonium chloride (Riedel-de Haën, Germany), were used for preparation of buffer solutions of pH 4, 7 and 10 which were used for calibration of the pH meter. The ionic strength adjustment buffer (TISAB) was prepared as follows: 57 mL of glacial acetic (Riedel-de Haën, Germany), 58 g of sodium chloride (UNICHEM, India), 7 g of sodium citrate(Riedel-de Haën, Germany), and 2 g of EDTA (FINKEM, India) were transferred into a 1 L round bottom flask and dissolved in 500 mL distilled water.

Then, the pH of the solution was adjusted in the range of 5.3 using 6 M sodium hydroxide, and then made to volume using distilled water [29].

3.4 Instrumentation and apparatus

Fluoride ion selective electrode (HI 4110, USA) was used to analyze the concentration of fluoride ion. GRANT GLS 400 shaker was used for shaking mixtures. pH meter (HANNA instruments, pH 211), Electronic balance (ADAM AFP-110L), Filter paper (5971/2 S&S Folded of 185mm), Oven (Model GENLAB WIDNES, England), Thermostatic water bath (Model Grant GLS400, England), Sieve (300 μm), Conical flasks, muffle furnace (model SX – 5 – 12) was used for firing of soils. Crucibles and, mortar and pestle were used for firing and crushing clay soils respectively.

3.5 Adsorbent preparation

The collected clay soil was dried at room temperature and ground using mortar and pestle. The collected tea leave was dried at room temperature and ground by using mortar and pestle. The ground tea leave was ashed at 450 °C for 3 hours by using a muffle furnace [30]. Three hundred gram of the air-dried and ground clay soil was thoroughly mixed with fifteen gram of the tea leave ash and pasted by adding distilled water. Three hundred gram of untreated clay soil was pasted in the same manner without adding tea leave ash. Both pastes were aged for 96 hours at room temperature in an open air and then fired at 570 °C for 3 hours [31] by using a muffle furnace. These fired clay soils were ground and the fraction with ≤ 0.3 mm particle size was used for adsorption of fluoride ion.

3.6 Adsorption study

Fluoride removal studies were carried out by using 2 g of FC or FC-TLA adsorbent and with 50 mL of fluoride ion solution under different conditions for two hours. The adsorption studies were conducted at a temperature of 25 ± 2 °C using thermostated water bath to determine the effect of pH, contact time and initial fluoride ion concentration on the adsorption of fluoride. The residual fluoride ion concentration was determined by using fluoride ion selective electrode. All experiments were carried out in triplicate, and the concentrations given are average values of the

triplicate analysis. Adsorption kinetics was studied by varying fluoride ion concentration in the test solution and the adsorbent dosage. The effect of temperature on the thermodynamic parameters was studied by varying the adsorption temperatures. The amount of adsorption at time t , q_t (mg/g), was calculated using the following relation:

$$q_t = \frac{(C_0 - C_t)V}{W} \dots \dots \dots (8) \quad [32]$$

Where C_t (mgL⁻¹) is the liquid phase concentrations of fluoride ion at any time t , C_0 (mgL⁻¹) is the initial concentration of the fluoride ion in solution. V is the volume of the solution (L) and W is mass of the adsorbent (g).

The amount of equilibrium adsorption, q_e (mg /g), was calculated using the formula.

$$q_e = \frac{(C_0 - C_e)V}{W} \dots \dots \dots (9) \quad [33]$$

Where C_0 and C_e (mgL⁻¹) are the liquid-phase concentrations of fluoride ions initially and at equilibrium

The percentage adsorption of fluoride ion in the solution was calculated by using the following equation.

$$\% \text{ adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100 \dots \dots \dots (10) \quad [34]$$

Where C_0 and C_e (mgL⁻¹) are the initial and equilibrium concentrations of the fluoride ion respectively.

3.6. 1 Effect of pH on adsorption

The effect of pH on adsorption of fluoride was studied between pH 4 - 9. This was done by using 2 g FC and FC-TLA with 50 mL of 30 mg/L fluoride ion solution in 250 mL conical flask. The pH of each solution was adjusted to the desired value by drop wise addition of 0.1 M HCl and/or 0.1 M NaOH. The conical flasks containing the mixture were kept in a thermostatic water

bath and shaken at 150 rpm and 25 ± 2 °C for 2 hours. The adsorbents were removed from the solution by filtration. The residual fluoride ion concentration in the filtrate solution was analyzed. The pH at which maximum adsorption occurred was taken as the optimum pH.

3.6.2 Effect of contact time on adsorption

The adsorptions of fluoride by FC and FC-TLA were studied at various time intervals (15-120 min) and at a concentration of 30 mg/L for fluoride ion. This was done by using 2 g of each of the adsorbents and 50 mL of 30 mg/L of fluoride ion solutions at the optimum pH obtained. The mixture was kept in a thermostatic water bath and shaken at 150 rpm at 25 ± 2 °C for various periods of time. The solution in the flask was filtered at different interval of time from the first to the last flask and the residual fluoride ion concentration was determined.

3.6.3 Effect of adsorbent dose on adsorption

The adsorption of fluoride ion by FC and FC-TLA at different adsorbent doses (1–4 g) and fluoride concentration of 30 mg/L was investigated. This was done by adding 1, 2, 3 and 4 g of the adsorbents into each flask and 50 mL of 30 mg/L of fluoride ion solutions at optimal pH and contact time. The flasks were kept in a thermostatic water bath and shaken at 150 rpm and a temperature of 25 ± 2 °C. FC and FC-TLA were removed from the solution by filtration and the concentration of residual fluoride ion in each solution was determined.

3.6.4 Effect of initial concentration on adsorption

Batch adsorption study of fluoride ion was carried out using a concentration range of 10 to 125 mg/L fluoride. This was done by using 2 g of the two adsorbents into each of the flask and 50 mL of fluoride ion solutions at optimal pH and contact time. The flasks were kept in a thermostatic water bath and shaken at 150 rpm and 25 ± 2 °C. The FC and FC-TLA were removed from the solution by filtration and the concentration of residual fluoride ion in each solution was determined.

3.6.5 Effect of temperature on adsorption

Batch adsorption process was studied by varying temperatures between 25 and 55 °C at an interval of 10 °C in order to investigate the effect of temperature on the adsorption process. This

was done by using 2 g of both adsorbents with 50 mL of 30 mg/L of fluoride ion solutions at the optimum pH and contact time obtained.

3.6.6 Application of the developed method for real sample

Batch adsorption process was studied for real sample, (groundwater) which was collected from Jimma town around Jimma University specialised Hospital to check whether the developed method is applicable for defluoridation of drinking ground water at the optimum conditions.

4 Results and Discussions

4.1 Effect of pH

The pH of the aqueous solution is an important parameter that affects the adsorption of fluoride ion on a clay surface. The effect of pH on the adsorption efficiency of fluoride by FC and FC-TLA was studied in the pH range of 4 – 9. The results obtained are shown in figure 1.

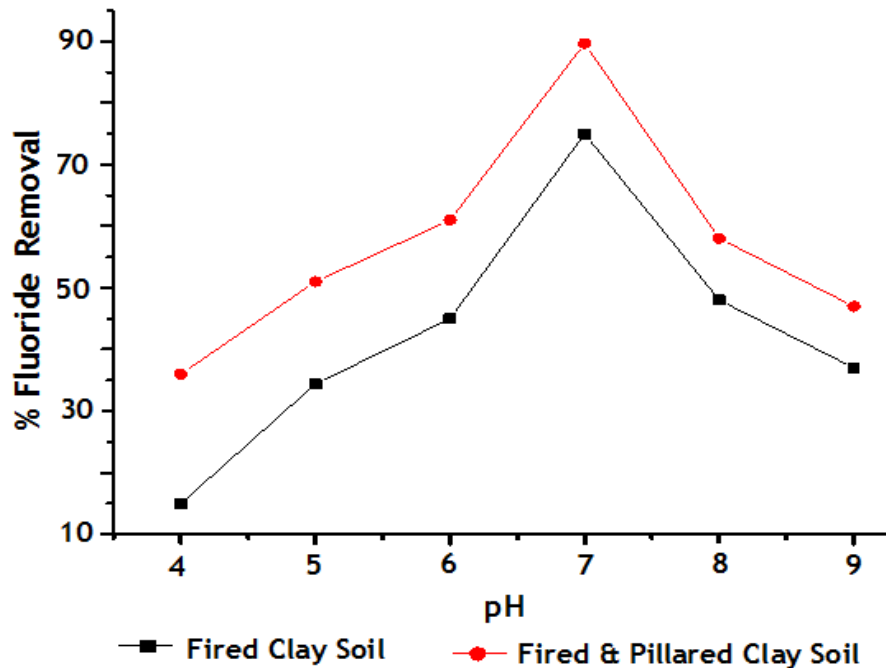


Figure 1: Effect of pH on adsorption of fluoride by FC and FC-TLA (Initial concentration of fluoride ion = 30 mg/L, adsorbent dose = 2 g, contact time = 120 min, agitation speed = 150 rpm and temperature = 25 ± 2 °C).

As shown in figure 1 the pH of the solution in which adsorption is taking place has a significant effect on the adsorption efficiency of the adsorbents. Maximum adsorption of fluoride was found to be 75% for FC and 90% for FC-TLA at pH 7. Percentage removal of fluoride by both adsorbents was found to increase from pH 4 to 7 and then decreased sharply as the solution's pH increased above 7. In acidic medium fluoride reacts with hydrogen ion and forms hydrofluoric acid which is weakly ionizable and reduces availability of free fluoride ion for adsorption. In

alkaline conditions, lower adsorption may be due to the competition of OH^- ions with F^- ions for adsorption because of similarity in F^- and OH^- in charge and ionic radius [35].

4.2 Effect of contact time

The progression of adsorption of fluoride with time was studied by measuring the amount of fluoride adsorbed at different contact time and the results obtained are depicted in figure 2.

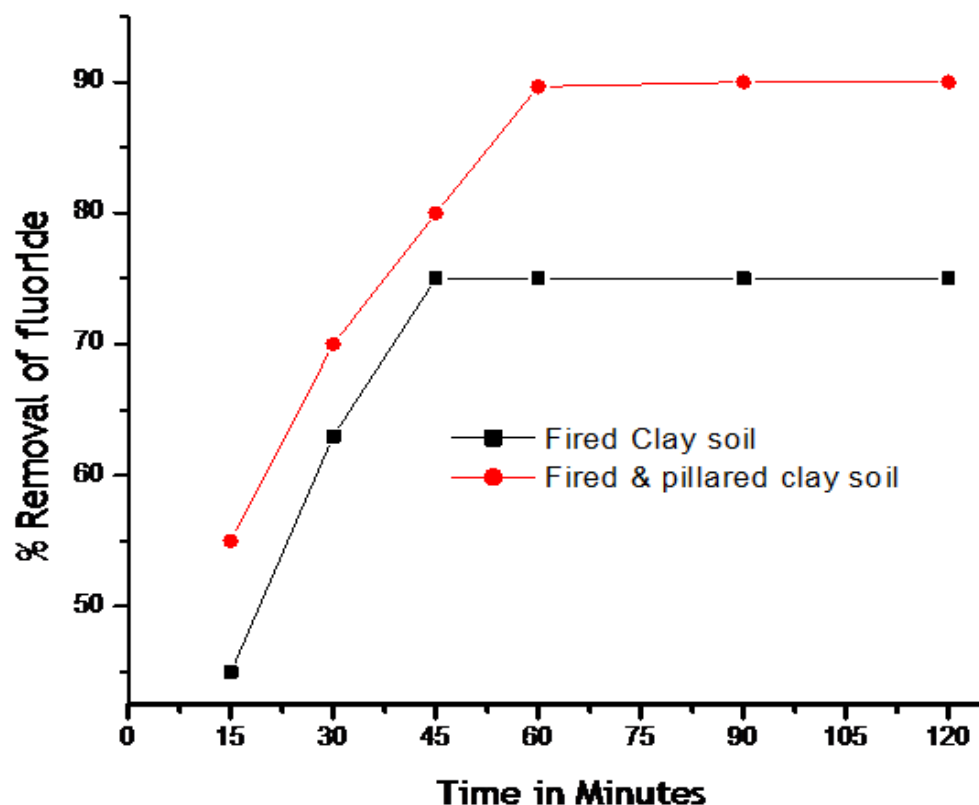


Figure 2: Effect of contact time on the adsorption of fluoride onto FC and FC-TLA (Initial concentration of fluoride ion = 30 mg/L, adsorbent dose = 2 g, pH= 7 agitation speed = 150 rpm and temperature = $25 \pm 2^\circ\text{C}$).

The fluoride adsorption efficiency of FC-TLA was found to increase linearly up to 60 minutes and remained constant from then on. While that of FC was found to increase up to 45 minutes and remained constant at higher contact time than 45 minutes. It was assumed that the equilibrium time is that at which the curves appear nearly parallel to the time axis. The high rate of removal at initial stage might be due to the fact that initially all adsorption sites were vacant

and the solute concentration gradient in the first parts of the solution was high. Later, the fluoride uptake rate by adsorbent had decreased significantly, due to the decrease in number of adsorption sites. The sorption rapidly occurs and normally controlled by the diffusion process from the bulk to the surface. Similar results were reported for adsorption of fluoride from aqueous solution onto tamarind seed, an unconventional biosorbents [36].

4.3 Effect of adsorbent dose

The effect of adsorbent dosage on the adsorption of fluoride was studied at a solution pH = 7 and, contact time of 45 min and 60 min for FC and FC-TLA respectively. The results obtained are depicted as percentage removal of fluoride versus adsorbent dosage in figure 3.

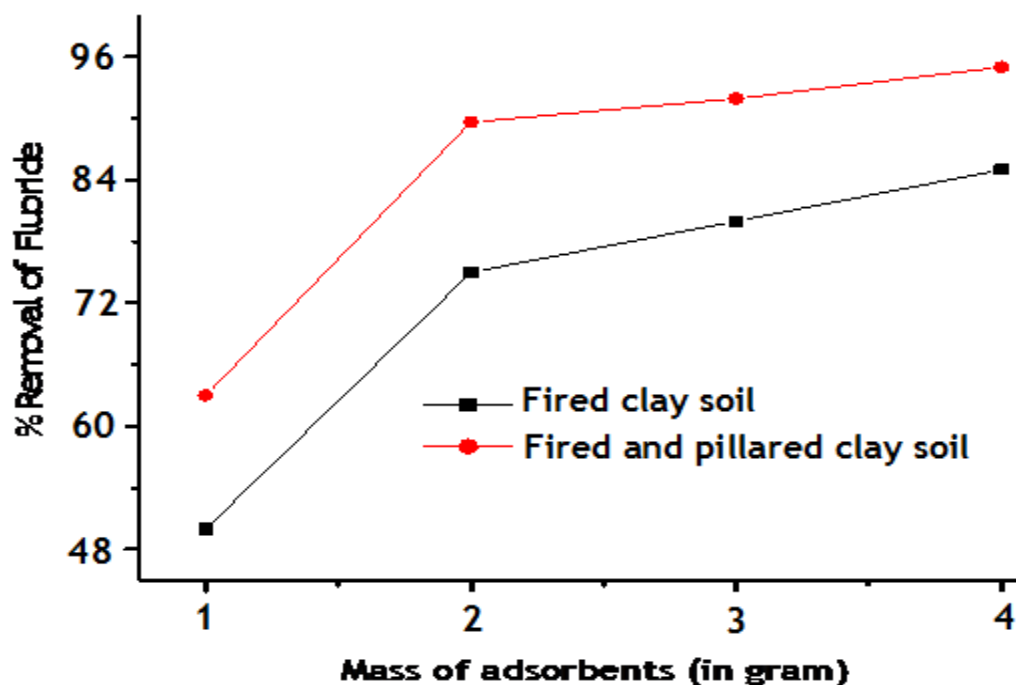


Figure 3: Effect of adsorbent dose on adsorption of fluoride onto FC and FC-TLA (Initial concentration of fluoride ion = 30 mg/L, pH= 7 contact time 45 min for FC, 60 min for FC-TLA, agitation speed = 150 rpm and temperature of 25 ± 2 °C).

The removal of fluoride increased from 50% to 85% for 1.0 – 4.0 g of adsorbent dosage for FC and 63 to 95% for FC-TLA. However, it can be seen from figure 3 that after 2 g of adsorbent

dose, there was no significant change in percent fluoride removal by both adsorbents. The non significant change in removal of fluoride as mass of adsorbent increase might be due to decrease in surface area of adsorbents [37]. So, these amounts of doses were used for further study.

4.4 Effect of initial fluoride concentration

The influence of adsorbate concentration was studied by using the concentration of fluoride solution having 10, 25, 30, 50, 75, 100 and 125 mg/L of fluoride ion. The results obtained are depicted in figure 4.

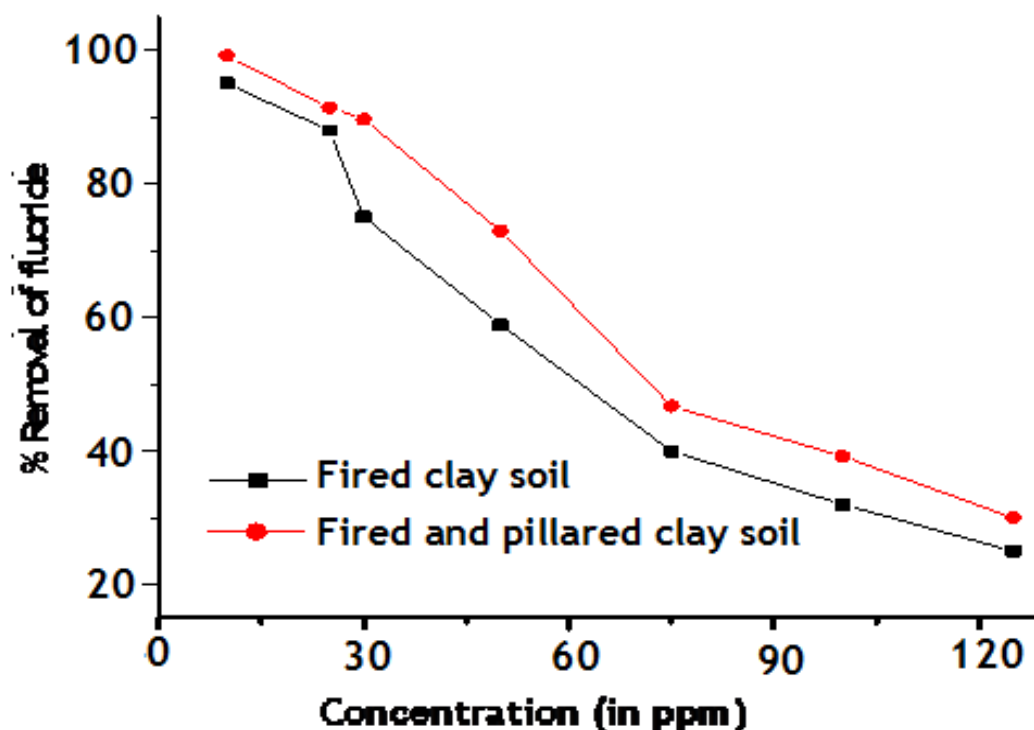


Figure 4: Effect of Initial fluoride ion concentration on adsorption efficiency of fluoride onto FC and FC-TLA) ($pH= 7$ contact time = 45 min for FC, 60 min for FC-TLA, adsorbent dose = 2 g, agitation speed = 150 rpm and temperature $25 \pm 2 ^\circ C$).

At 10 mg/L there was 95% and 99% removal of fluoride ion by FC and FC-TLA respectively. At 30 mg/L 75% and 90% of fluoride ion was removed from the solution by FC and FC-TLA respectively. At high concentration (125 mg/L) there was 25% removal by FC and 30% removal by FC-TLA.

At lower concentrations, (10 mg/L) all fluoride ions present in the solution would be adsorbed on to the binding sites because of minimum competition among these fluoride ions for the binding site and then facilitated more than 95% adsorption for FC and 99% adsorption for FC-TLA. At higher concentration (125 mg/L), more fluoride ions are left unadsorbed in the solution due to the saturation of binding sites. This appears due to the increase in the number of ions competing for available binding sites of the adsorbents [38].

4.5 Effect of temperature

The effect of temperature was studied by varying the solution temperature between 25 and 55°C at an interval of 10 °C. This was done by using 2 g of FC and FC-TLA with 50 mL of 30 mg/L of fluoride ion solutions at the optimal pH and contact time. The results obtained are presented in figure 5.

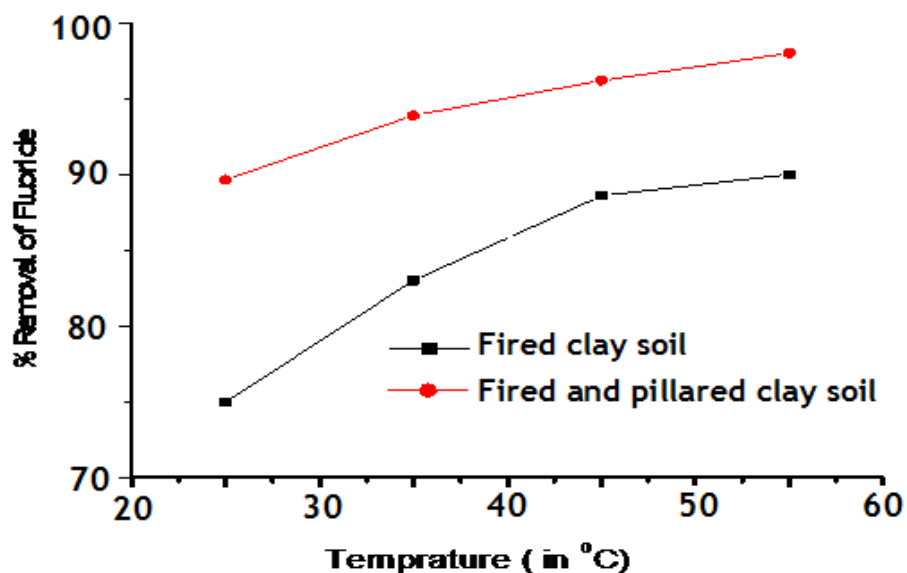


Figure 5: Effect of temperature on adsorption of fluoride onto FC and FC-TLA (Initial concentration of fluoride ion =30 mg/L, pH= 7, contact time 45 min for FC and 60 min for FC-TLA and adsorbent dose = 2 g and agitation speed = 150 rpm).

With an increase in temperature from 25 to 55 °C a successive rise in the percent adsorption of fluoride from 75 to 90% by FC was observed. While for the FC-TLA adsorbent the rise in percent adsorption of fluoride for the same rise in temperature was from 90 to 98 %. It can be assumed that increase in temperature strongly increased the energy of the ions. More fluoride ions could therefore interact effectively with the surface of the adsorbents for adsorption to occur resulting in higher percentage of fluoride removal from solution [39]. The enhancement of fluoride adsorption capacity with temperature is attributed to the possible increase in the number of active sites available for adsorption on the surface. The kinetic energy of fluoride ion increased with increasing temperature of solution. The collision frequency between adsorbate and adsorbent increased and hence the greater the adsorption on the surface of the adsorbent particles [40]. The amount of fluoride ion that was adsorbed increased at higher temperatures. These results indicated the adsorption mechanism of fluoride ion onto FC and FC-TLA is an endothermic reaction [41].

4.6 Application of the developed method for real sample

Ground water was obtained from six wells which are found around Jimma University Specialized Hospital. The maximum concentration of fluoride in the water was found to be 5 mg/L. Water which has 5 mg/L of fluoride was taken and 11.05 mg of NaF was dissolved in 500 mL of it to increase the concentration of fluoride in it to 15 mg/L.

Batch adsorption experiment was done on this real sample at adsorbent dose of 2 g, contact time of 45 min for FC and 60 min for FC-TLA; temperature of 25 ± 2 °C and agitation speed of 150 rpm and pH was 7. FC has removed 90.8% where as FC-TLA removes 96.5% of fluoride in the water sample. This shows that the applicability of the developed method for treatment of fluoride in ground water and from these we can conclude that our new adsorbent is good to defluoridate water which has high fluoride concentration.

4.7 Adsorption isotherms

Isotherm studies are essential to interpret the adsorption process adequately. Several models have been used to describe experimental data for adsorption isotherms. However, among these, the Langmuir and Freundlich isotherms are the most appropriate models for this study. According to the Langmuir isotherm, adsorption occurs at homogenous sites and forms a monolayer. In other words, once adsorbate is attached to a site, no further adsorption can take place [42]. . The linear form of Langmuir isotherm equation is given in equation (5). The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L which is given in equation (6). The values of separation factor R_L can be summarized as shown in Table 1.

Table 1: Separation factor

Value of R_L	Types of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption properties consisting of heterogeneous surface of the adsorbent. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption and is expressed by:

$$q_e = K_f C_e^{\frac{1}{n}} \dots \dots \dots (10) \quad [26]$$

The linear form of Freundlich isotherm is given in equation (7)

Where q_e is the amount adsorbed at equilibrium (mg/g), K_f is the Freundlich constant, $1/n$ is the heterogeneity factor which is related to the capacity and intensity of the adsorption, and C_e is the equilibrium concentration (mgL^{-1}). The values of K_f and $1/n$ can be obtained from the slope and intercept of the plot of $\log q_e$ against $\log C_e$. However, present investigation attempted to analyze the above mentioned isotherm parameters at 25 ± 2 °C and the model parameters are listed in table 2. The correlation coefficients, R^2 were calculated by fitting the experimental equilibrium data for the fluoride ion by FC and FC-TLA using both Langmuir and Freundlich isotherms, and are presented in Table 2.

These results clearly show that the adsorption of fluoride on FC and FC-TLA fits well with the Freundlich model. The fact that the Freundlich model is a good fit to the experimental adsorption data suggests physical adsorption as well as a heterogeneous distribution of active sites on the surface of both adsorbents. The observed correlation coefficients for Freundlich isotherms were 0.930 for FC and 0.998 for FC-TLA. The other Freundlich constant, n , is a measure of the deviation of the adsorption from linearity. If the value of n is equal to unity, the adsorption is linear. If the value of n is below unity, it implies that the adsorption process is unfavourable, and if the value of n is above unity, adsorption is favourable [43]. In the present study, the value of n at equilibrium was above unity, suggesting favourable adsorption. Furthermore, the values of the dimensionless factor, R_L , were between 0 and 1. This also suggested favourable adsorption between fluoride and FC as well as FC-TLA.

Table 2 Results of isotherm models for the adsorption of fluoride onto FC and FC-TLA at 25 ± 2 °C

Adsorbents	Langmuir isotherm			Freundlich isotherm			R_L at 30 mg/L
	q_m (mg/g)	b_L	R^2	k_f	$1/n$	R^2	
FC	25.64	0.053	0.816	2.21	0.707	0.930	0.386
FC-TLA	34.48	0.230	0.979	0.993	0.484	0.998	0.126

4.8 Adsorption kinetic studies

For any adsorption system, study of chemical kinetics is very important so as to determine the rate constants for the reaction and to know how quickly or slowly the reaction is proceeding. In order to evaluate the kinetic parameters, Pseudo first order, Pseudo second order and intra particle diffusion models were implemented to analyze the experimental data [44]. The pseudo first order is given in equation (1).

From the plots of $\log (q_e - q_t)$ versus t , k_1 can be calculated from the slope and theoretical q_e can be obtained from intercepts [45]. Pseudo second order equation was given in equation (3). The linear plots of t/q_t versus t determine $1/q_e$ as slope and $1/K_2q_e^2$ as intercepts. The linear plots of pseudo second order model is shown in figure 8 and 9.

The correlation coefficient, R^2 of pseudo first order kinetics was 0.797 for FC and 0.925 for FC-TLA but the calculated q_e (mg/g) values obtained from Pseudo first order kinetics did not agree well with the experimental (mg/g) values were shown in Table 3. Thus it can be concluded that it is not appropriate to use the Pseudo first order kinetic model to predict the adsorption kinetics of fluoride onto FC and FC-TLA for the entire adsorption period.

On the contrary, the correlation coefficients, R^2 for the second order kinetic model were almost fits better than that pseudo first order for all the concentrations signifying the applicability of the model. Moreover, the calculated q_e (mg/g) values obtained from Pseudo second order kinetics were in good agreement with the experimental (mg/g) values (Table 3). Thus it is appeared that the system under study is more suitably described by pseudo second order kinetics which was based on the assumption that the rate limiting step may be physisorption due to the presence of weak forces of attraction between adsorbent and adsorbate. The pseudo second-order kinetics model has been successfully applied to several adsorption systems as reported by [46].

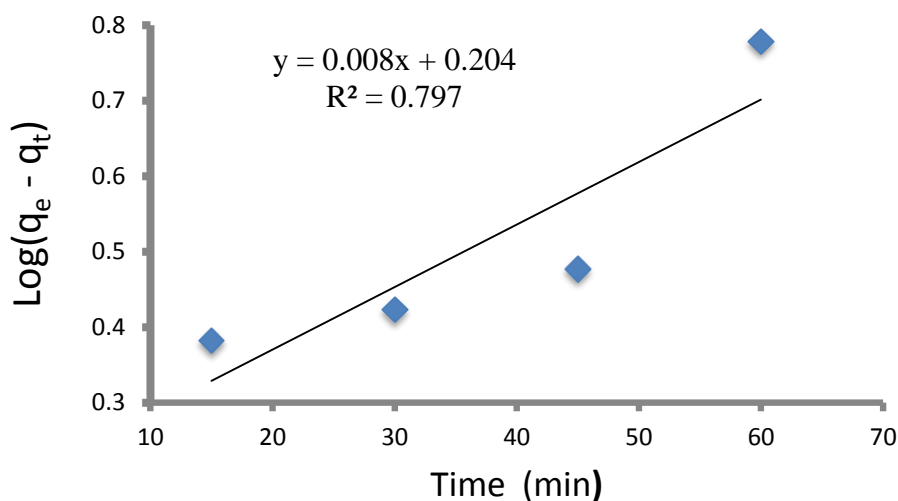


Figure 6 Pseudo-first-order kinetics plot for the adsorption of fluoride onto FC

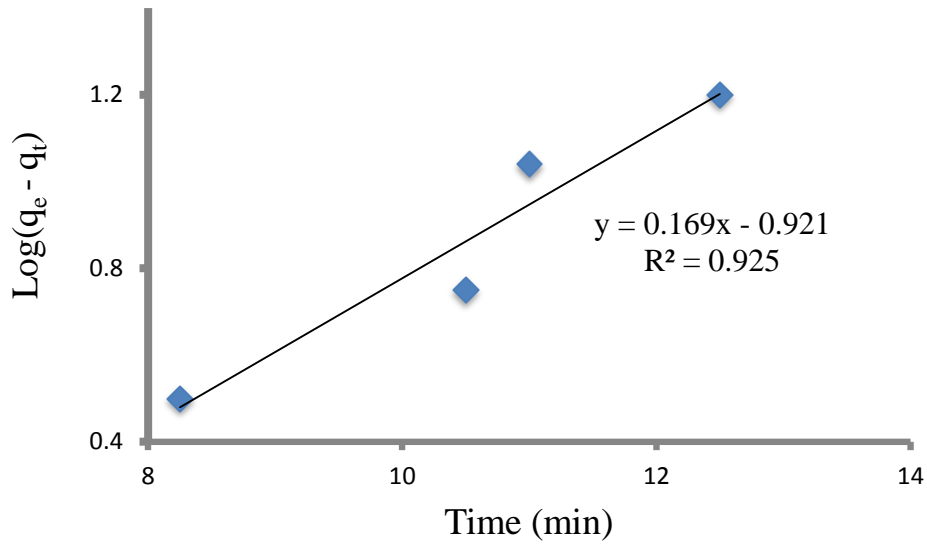


Figure 7 Pseudo-first-order kinetics plots for the adsorption of fluoride onto FC-TLA

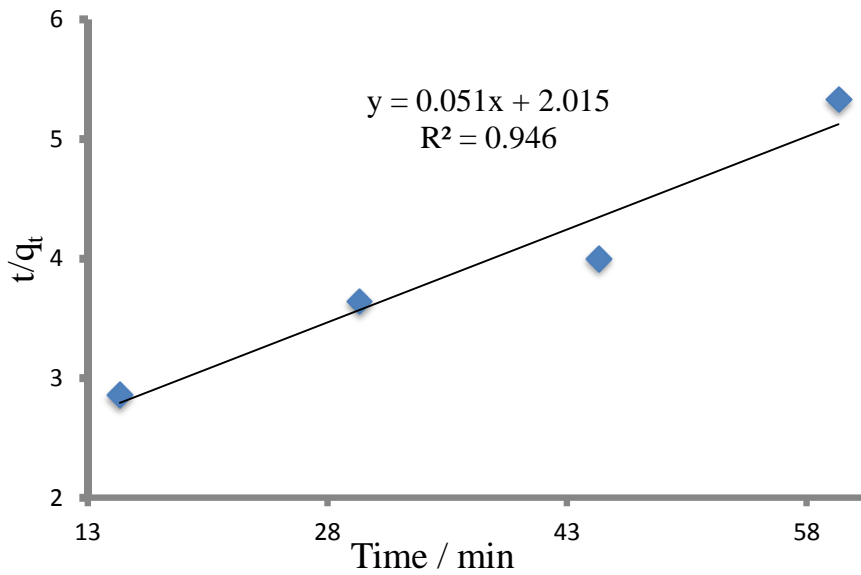


Figure 8 Pseudo-second-order kinetic plot for the adsorption of fluoride onto FC

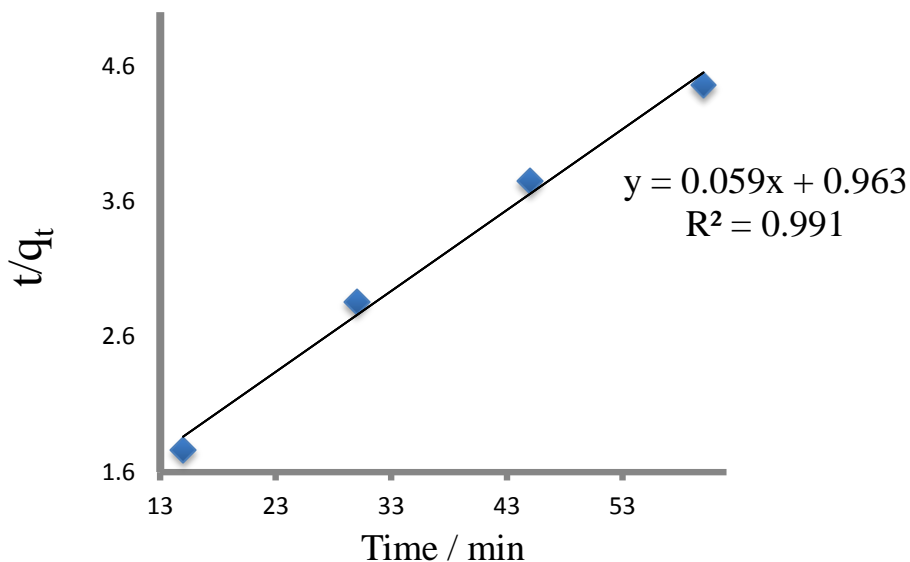


Figure 9 Pseudo-second-order kinetic plots for the adsorption of fluoride onto FC-TLA

Table 3: Kinetics parameters for the adsorption of fluoride onto FC and FC-TLA at 25 ± 2 °C

Adsorbents	Pseudo-first order				Pseudo-second order		
	q_e exp. (mg/g)	q_e Cal.	$k_1 (\times 10^{-2} \text{ min}^{-1})$	R^2	q_e Cal.	$k_2 (\frac{\text{mg}}{\text{g} \cdot \text{min}})$	R^2
FC	8.02	1.5	3.05	0.797	7.99	1.23	0.946
FC-TLA	12.03	2.04	5.05	0.925	12.35	3.92	0.991

The amount of fluoride adsorbed per unit mass of adsorbent at time t , q_t , as a function of the square root of the contact time, $t^{1/2}$, was examined using the intra particle diffusion model which is based on the theory proposed by Weber and Morris and given by the following equation.

$$q_t = k_d t^{1/2} \dots \dots \dots (11) \quad [46]$$

Where k_d (mg/g/min^{1/2}), is the intra particle diffusion coefficient, was calculated from the slope of the linear portion of curves and C (mg/g), is intra particle diffusion constant i.e. intercept of the line (mg/g). It is directly proportional to the boundary layer thickness. It is assumed that, the

larger the intercept, the greater the contribution of the surface adsorption in the rate-controlling step. The calculated intra particle diffusion coefficient values are listed in Table 4.

Intra particle diffusion plays a significant role in controlling the kinetics of the adsorption process, if the plot of q_t versus $t^{1/2}$ yields a straight line passing through the origin, with the slope giving the rate constant, k_d . If the lines do not pass through the origin it is indicative of some degree of boundary layer control and this further shows that the intra-particle diffusion is not the only rate limiting step, but other kinetic models may also control the rate of adsorption [47].

The plots of intra-particle diffusion in figure 10 and 11 showed that, the lines did not pass through the origin. This implied that the rate limiting process is not only governed by intra particle diffusion. Some other mechanism along with intra particle diffusion was involved for the whole adsorption process. Similar findings were reported by other researcher [46].

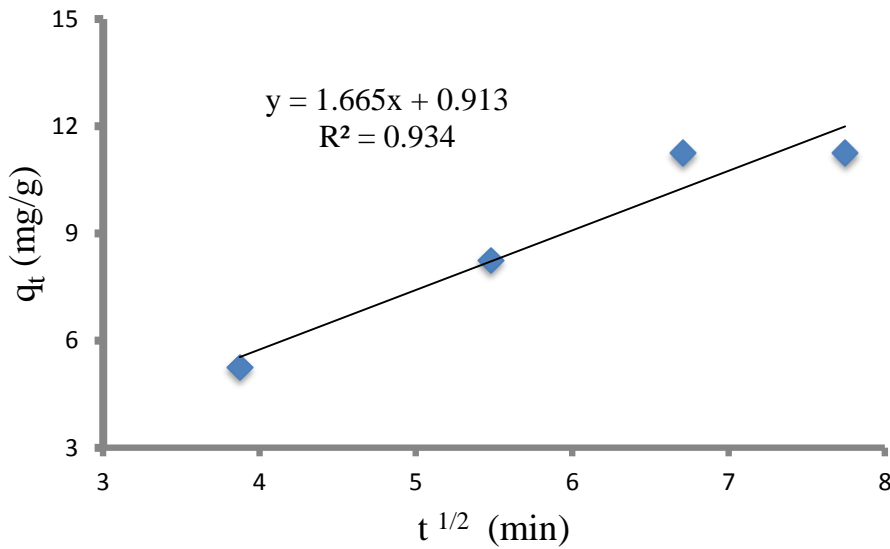


Figure 10 Intra particle diffusion curve for adsorption of fluoride onto FC at 25 ± 2 °C temperature

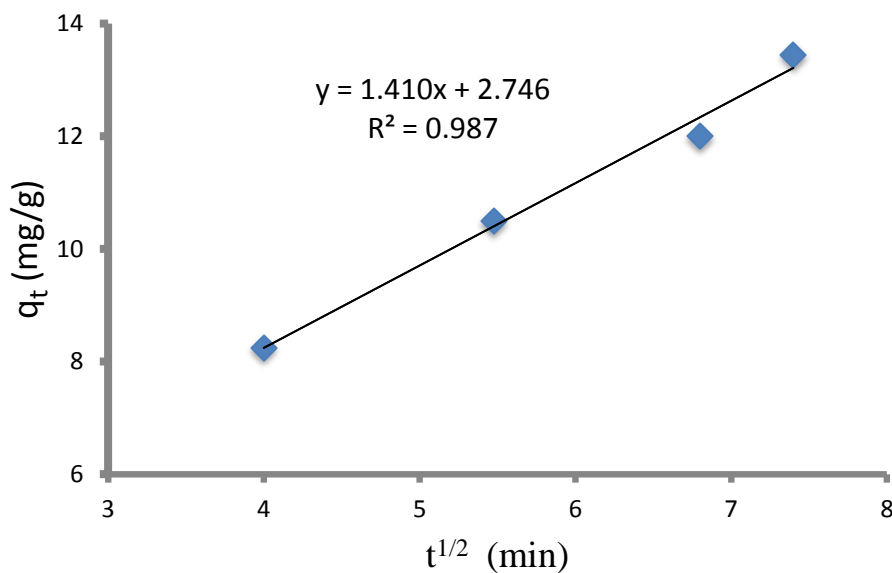


Figure 11 Intra particle diffusion curve for adsorption of fluoride onto FC-TLA at 25 ± 2 °C temperature

Table 4: Intra particle diffusion rate study for adsorption onto FC and FC-TLA at 25 ± 2 °C temperature

Adsorbent	K_d (mg/g/min ^{1/2})	C (mg/g)	R^2
FC	1.665	0.913	0.934
FC-TLA	1.410	2.746	0.987

4.9 Comparison of fluoride adsorption onto different adsorbents

The adsorption capacity of the adsorbents for the adsorption of fluoride has been compared with those of others reported in the literature and the values of adsorption capacity as presented in Table 5. The experimental data of the present investigation were compared with reported values. Results of our investigation revealed that FC-TLA has the highest percent adsorption and adsorption capacity

Table 5 Comparison of F⁻ adsorption capacity data in mg g⁻¹ for different soils and clays.

Conditions: [F⁻] initial = 10 mgL⁻¹, 1 g clay, pH = 5 - 7, equilibration time > 2h

Sorbent	Sample name and description	Adsorption capacity mg.g⁻¹	Reference
activated alumina	Type 504C, Fluka	0.5	[19]
goethite /illite	Tertiary soil Shanxi China	0.23	[49]
goethite / kaolinite	SLV Sri Lanka	0.35	[19]
Kaolinite	Acid soils USA	0.17–0.25	[20]
Kaolinite	Potter's clay, 30% Al ₂ O ₃ 1106 White St Thomas	0.12	[50]
Kaolinite	Clay pots Ethiopia	0.07	[51]
Fired clay soil	FC	0.30	This work
Fired clay soil pillared with tea leave	FC-TLA	0.495	This work

5) Conclusion and Recommendations

This study investigated that the adsorption fluoride on fired clay soil and fired clay soil pillared with tea leaves ash components. The experiments were carried out at initial pH of 7 of the solution to ensure true adsorption. The adsorption was found to be strongly influenced by pH, contact time and temperature. Equilibrium was attained very quickly within 45 minutes for FC and 60 minutes for FC-TLA. Both Freundlich and Langmuir models were used to fit the data and estimate model parameters but the overall data is better fitted by Freundlich isotherm at the studied temperature range reflecting surface heterogeneity of FC and FC-TLA. The kinetic studies conducted using the Weber and Morris equation showed that the adsorption mechanism involves intra-particle diffusion but it was not the fully operative mechanism in the adsorption of fluoride by FC and FC-TLA. The pseudo-second order kinetic model was found to be a better fit for the adsorption of fluoride by FC and FC-TLA.

The result indicates that, the findings will be helpful up to a great extent for treating of fluoride contaminated waters and at the same time it is economically feasible and environmentally friendly material which can be employed successfully for separation of fluoride from aqueous in industrial scale. It can be concluded that FC-TLA is a good and cheap adsorbent with high potential for the adsorption and removal of fluoride from fluoride contaminated water and could therefore serve as effective and efficient biomass for treating drinking waters in terms of high adsorption capacity. In addition it will help to enable people to use environmentally friendly and easily operational methods in developing countries as alternatives of advanced technologies. Further, the study initiates the community to due attention for treatment of fluoride contaminated water.

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