Synthesis of Hydroxyapatite from Eggshell

for defluoridation of water by adsorption

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Approval of Board of Examiners

We, the undersigned, members of the Board of Examiners of the final open defense by Kifle Workeneh read and evaluated his thesis entitled " synthesis of hydroxyapatite from eggshell for defluoridation of water by adsorption" and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement of the Degree of Master's in Chemistry

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This is to certify that the thesis entitled **"SYNTHESIS OF HYDROXYAPATITE FROM EGGSHELL FOR DEFLUORIDATION OF WATER BY ADSORPITION"** submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry has been carried out by Kifle Workeneh Id. No GSU/0499/06, under our supervision. Therefore, we recommend that the student has fulfilled the requirements and hence hereby he can submit the thesis to the department.

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List of Abbreviation

EDTA……...Ethylenediamine tetrameric acid

FA…… Fluoroapatite

FSE…… Fluoride Selective Electrode

FT-IR…….Fourier Transform Infrared Spectroscopy

HA…… Hydroxyapatite

HA…….Hydroxyapatite powder

ISE ……Ion Selective Electrode

ISO…… International Standard Organization

nHAp …… Natural hydroxyapatite

HAp…… Synthetic hydroxyapatite

TGA…… Thermogravimetric Analysis.

TISAB …… Total Ionic Strength Adjustment Buffer.

TISAB…… Total ion strength adjustment buffer

WHO ……. World Health Organization

Abstract

The present study deals with fluoride ion removal from aqueous solution by hydroxyapatite adsorbent synthesized from waste eggshell as calcium precursor and phosphoric acid through wet chemical precipitation technique. The prepared adsorbent was characterized using XRD, FT-IR and TGA techniques. Batch adsorption studies were carried out to investigate the effect of initial pH of the solution, contact time, adsorbent dose and initial fluoride concentration on the adsorption capacity of hydroxyapatite. The fluoride removal efficiency was determined using fluoride ion selective electrode. Fluoride adsorption was found to be pH dependent and 98.8%.of fluoride was removed at pH 3.0 but, at pH ~7.0, 85% of fluoride was removed. Both the Langmuir and Freundlich models were tested for the adsorption isotherm studies and the experimental results indicated that the Langmuir model was more favorable for the removal of fluoride and the reaction followed pseudo second order kinetics. The synthesized hydroxyapatite crystal has also about 81% removal efficiency for the tested real water samples.

Key Words: hydroxyapatite, defluoridation, adsorption, calcination, kinetics

1. INTRODUCTION

1.1. Background of the study

Water is one of the basic needs of life on earth which may be contaminated by natural sources or industrial effluents. One of such contaminant is fluoride, which exists in different chemical forms in combination with other elements. It is distributed widely in nature, both in inanimate and living things [1]. Though fluoride is an essential constituent, depending on its level of fluoride in drinking water, it can be either beneficial or detrimental to human health [2]. When the concentration of fluoride in drinking water is above 1.5 mg/L, it results in dental, skeletal, and non-skeletal fluorosis due to its strong attraction by positively charged calcium ion in teeth and bones [3].

The East African Rift Valley crosses Ethiopia, Kenya, Tanzania, and Mozambique, where the same go eugenic water-related problem with fluoride occurs. In Kenya, the Catholic Diocese of Nakuru (CDN) is working with success since more than 10 years' work on bone char technology to remove fluoride from water. In collaboration with Eawag (Swiss Institute for aquatic research), Heks (Swiss Interchurch Aid) and OSHO (Oromo Self Help Organization), this technology was introduced in Ethiopia in 2007 [4]. The coverage is still not much with regards to the problem in the Ethiopian Reify valley. In Kenya, there are community filters and Household filters in different designs available, while in Ethiopia, there is only one community filter and one type of household filter. The accessibility of safe water in rural Ethiopia is still only 14% of the whole population, and only 8% within a walking distance of 30 minutes [5]. Ethiopia is one of the 23 countries in the world, where a significant number of its population suffers from the toxic effects of high levels of fluoride in drinking water. The toxic effect of the excess amount of fluoride in the drinking water of several towns in the Ethiopian Rift Valley has been in evidence since 1970. This was due to the fact that the people in these areas were accustomed to drinking water that contains about 33 mg/L [6]. Hence, there is a need for the development of simple and cost-effective methods to remove the excess fluoride from the drinking water.

Conventional methods for fluoride removal are membrane filtration; precipitation, ion-exchange/adsorption, and distillation have been used for fluoride removal. Most of these methods have high operational and maintenance cost, low fluoride removal capacities, lack of selectivity for fluoride, undesirable effects on water quality, generation of large volumes of sludge and

complicated procedures involved in the treatment. Among these methods, adsorption is the most effective and widely used method because it is universal, has a low maintenance cost, and is applicable for the removal of fluoride even at low concentrations [7]. Thus, it is important to explore low-cost adsorbents for the adsorption of fluoride from aqueous medium. Various low-cost materials such as activated alumina, clay, soil, bone char, lightweight concrete, fly ash and other materials have been tested for removing fluoride from drinking water but the fluoride adsorption capacities of those materials are not high enough for wide application [8]. Suppose, bone char is a commonly used adsorbent in developing countries for defluoridation of drinking water, mainly due to economic reasons, and has been studied by several researchers it faced many Limitation regarding its application despite the encouraging results obtained from high-quality bone char materials, this adsorbent has major disadvantages. The hygienic problem and the low adsorption capacity of the poor-quality bone char, which are a direct consequence of the crucial preparation method, as well as cultural and religious objections, are the major barriers that limit its usage on a large scale throughout the world [9]. For these reasons, considerable number of studies have dealt to search and research to get various types of other adsorbent materials, of which synthetic hydroxyapatite remains as the main candidate due to its identical chemical composition with bone, non-toxicity, availability and high defluoridation capacity [10] [11] Recent research indicate that calcium based materials like HAp have better defluoridation capability and the defluoridation efficiency is greatly size dependent on synthetic hydroxyapatite [12].

Many researchers have tried to synthesize the HA through various routes. Some of the conventional routes of producing HA include wet precipitation method, hydrothermal technique, Low-temperature synthesis, and sol-gel technique. In many of the techniques, final HA phase is obtained only after calcination at 1200˚C, whereas some techniques are unreasonably time-consuming and at elevated temperature end with the formation of undesirable anions like CO_3^{-2} and CaO [12]. Among this, wet chemical precipitation method by far more advantageous for its simplicity and cost-effective [13]

Basically, HA can be synthesized either from biowaste like coral [14] and seashell [15] or from calcium and phosphate source precursor. Few researchers have also used eggshell for chemically synthesizing HA [16]. A huge number of eggshells are left daily, which are of no use and produce

waste. These eggshells support microbial action and lead to polluting the environment. Therefore, this work was targeted to synthesize Hydroxyapatite powder from eggshell and phosphoric acid through wet chemical precipitation. Further, the synthesized HA powder samples were characterized by XRD for crystal size and morphology, FTIR, for functional group identification. Finally, the HAp was tested for its defluoridation capacity in laboratory prepared fluoride solution (water) and row water that actually the society use around Adama city. The Analysis was done on the bases of deformation efficiency of the synthesized HA powder. The removal efficiency of the nHAp (obtained from eggshell) were compared with HAp (obtain from chemical precursors) and bone char to assure that HAp is a low-cost adsorbent that has good potential to remove fluoride. Effects of various operating parameters that may affect the adsorption process like the effect of pH, the effect of the initial concentration of adsorbate and the amount of adsorbent (HAp) used were examined. The recommendation was given for its further investigation and application on groundwater Treatment.

1.2. Statement of the problem

Fluoride is one of the chemical elements that is found most frequently in groundwater and has become one of the major toxicological environmental hazards globally [17]. The formation of fluoride is based on the interaction of element fluorine with the minerals present in soil and rocks. Even though fluoride is important for mineralization of hard tissues and bones, it can be detrimental to humans when exposed to elevated concentrations. Fluoride is used as an additive to drinking water in an attempt to prevent tooth decay, while this idea was rise to fear and suspicion. World Health Organization (WHO) and ISO: 10500 recommend that fluoride content in drinking water should be in the range of 1.0 to1.5 ppm. It is estimated that about 80% of diseases in the world are attributed to poor quality of drinking water, of which fluoride contamination in drinking water is responsible for 65 % of endemic fluorosis [18]. The actual number of people affected by fluorosis is not known, but according to the Ethiopian Ministry of Water Resources estimates, more than 11 million people in the Rift Valley region are highly vulnerable to fluoride related problems as they rely on drinking water sources having high fluoride concentrations [19] Though there are attempts to reduce the total fluoride concentration in potable waters, the mitigation activities in Ethiopia are still at the initial stages. One option to prevent fluorosis can be the use of alternate water sources like surface water, rainwater and less fluoride containing groundwater. In

cases where these alternatives are not available, or limited, like in the case of Ethiopian Rift Valley region, and where the groundwater to which communities at large depend on is often greater than 10 mg/ L Fluoride [20] defluoridation of drinking water is an alternative option remaining to prevent fluorosis [21]. Yet, periodic monitoring is required to avoid mixing of high fluoride feasible. The conventional rural Defluoridaion techniques like Nalgonda technique and Activated alumina generates a large amount of fluoride sludge [22]. Moreover, better and effective removal technologies like reverse osmosis, ion exchange, dialysis and electro dialysis, adsorption by commercial carbons, are costly and often just not feasible for that purpose. Thus, it is important to explore low-cost adsorbents for the adsorption of fluoride from drinking water.one of such effective law cost fluoride removal material is hydroxyapatite. Therefore, this study attempt was to synthesis hydroxyapatite from eggshell to test its deflourdation efficiency by adsorption.

1.3. Objectives of the study

1.3.1. General objective

- The main objective of this work is to synthesize hydroxyapatite powder from eggshell for Defluoridaion of drinking water by adsorption.

1.3.2. Specific objectives

- To characterize hydroxyapatite obtained from the eggshell.
- To investigate the removal efficiency of fluoride by hydroxyapatite.
- To Study the effect of contact time, pH, adsorbent dose and concentration of fluoride on adsorption.
- To study isotherm and kinetic phenomena for the adsorption process of fluoride by the synthesized hydroxyapatite.

1.4. The significance of the study

The study is primarily focused on the way how pure Hydroxyapatite powder can be produced from easily available raw material (eggshell) and phosphoric acid by most simple and versatile method known as wet chemical precipitation and, the research also attempt to assess an alternative potential Defluoridation material. Therefore, the study is significant to show the gap between the previous trend to use HA and the present status about the different application of hydroxyapatite to the next researchers.

1.5. The scope of the Study

This study was limited to the synthesis and characterization of HAp from eggshell for investigating the most economical and easily applicable technique for fluoride removal in Ethiopian rift valley.

2. LITERATURE REVIEW

2.1. Fluoride occurrence

Fluorine is the 13th most abundant naturally occurring element in the Earth's crust. Due to its very high reactivity, it is found chemically as fluoride (F-) in various rocks, commonly in Fluorite (CaF_2), Cryolite (Na_3AlF_6) and Fluorapatite ($Ca_5(PO_4)_3F$) [23]. Although these fluoride-bearing minerals are hardly soluble in water when conditions favor they do dissolve in polluted water or are found through human activities such as discharge by agricultural and industrial activities including fertilizer, steel, aluminum and glass manufacturing, and electroplating [24]. Generally, most groundwater sources have higher fluoride concentrations than surface water. As groundwater percolates through the weathered rock in the aquifers, it dissolves fluoride-bearing minerals, hence releasing fluoride into solution [23]. The floor of the East African Rift Valley is characterized by high hydrothermal activity, which accelerates the solubility of fluoride-bearing minerals such as fluorite and fluorapatite with high concentrations of fluoride in the groundwater. The level of fluoride in drinking water is a very important physicochemical factor, which must be considered when assessing water quality for human consumption. Based on current literature, fluoride has both beneficial and detrimental health effects depending on its concentration in drinking water [25]. As a trace element, fluoride is essential to the growth as well as the strengthening of teeth and bones [26], and in that, it is especially beneficial to young children below eight years of age. Low intake of fluoride could reduce the incidence of dental caries. In contrast, excess ingestion of fluoride can cause dental/skeleton fluorosis and increased blood pressure [27]. It has been reported that chronic ingestion of fluoride and its accumulation over a long period of time can bring about further complications (cancer, osteosclerosis and neurological impairment) [28]. In recognition of high levels of fluoride in drinking water to be a risk factor for fluorosis, the World Health Organization (WHO) has set the maximum permissible limit of fluoride in drinking water at 1.5 mg/L [29]. However, the recommended level to achieve maximum protection against dental caries and risk of fluorosis is in the range between 0.5 and 1 mg/L [27].

2.2. Fluoride adsorption mechanisms and its effect

Consumption of high amount of fluoride exposes to fluorosis, most probably due to its reaction with HAp Ca_{10} $(PO4)_6(OH)_2$, the main inorganic constituent of bones and teeth. Several studies

were conducted on the mechanism of fluoride adsorption onto HA particles [30]. In general, both physical adsorption originating from electrostatic interaction (eq. 1.1) and chemical adsorption from ion exchange (eq. 2 and 3) were proposed as the main driving force for fluoride uptake onto HAp surfaces [31].

$Ca_{10}(PO4)_6(OH)_2 + n\ F^-$---------- $Ca_{10}(PO4)_6(OH)_2 \ldots F_n$----------(1.1)

$Ca_{10}(PO_4)_6(OH)_2 + F^-$ ---------- $Ca_{10}(PO4)_6F$, ---------- (1.2)

$Ca_{10}(PO_4)_6(OH)_2 + 2F^-$ ---------- $Ca_{10}(PO_4)_6F_2 + 2OH^-$ (1.3)

Furthermore, it has been reported that the fluoridation at significantly high fluoride concentration could also take place on HAp dissolved surface phase to form calcium fluoride *(*CaF_2) as shown in Eq. 1.4

$Ca_{10}(PO4)_6(OH)_2+20F^-$ _____ $10CaF_2+ 6(PO4^{-3})+ 2\ OH^-$ ----------.(1.4)

Therefore, the above reaction indicated that fluorapatite is the resulting product of electrostatic interaction or ion exchange reaction. Fluorapatite, which has a very low solubility, is the compound of fluoride found in the mineral part of bones and teeth, and that plays a significant role in strengthening them if present in small quantities. However, at high fluoride concentration the conversion of a large amount of the hydroxyapatite into less soluble fluorapatite (Ksp, FA= 3.16 X 10^{-60}, Ksp, HA= 2.34 X 10^{-59}) in human favors the condition of making the teeth denser, harder and more brittle, also known as dental fluorosis and in extreme case skeletal fluorosis.

2.3. Fluorosis

The relationship between fluoride and fluorosis was first noted in the early part of the 20th century when it was observed that residents of certain areas of U.S.A. developed brown stains on their teeth. In the 1930's it was observed that the prevalence and severity of this type of mottled enamel were directly related to the amount of fluoride ingested [32]. Optimum fluoride concentration in drinking water may be defined as a one that arrests the prevalence of dental carries without causing a significant amount of fluorosis [33].

2.4. Symptoms of fluorosis

Dental fluorosis, which is characterized by discolored, blackened, mottled or chalky- white teeth, is a clear indication of overexposure to fluoride during childhood when the teeth were developing. These effects are not apparent if the teeth were already fully grown prior to the fluoride overexposure; therefore, the fact that an adult may show no signs of dental fluorosis does not necessarily mean that his or her fluoride intake is within the safety limit [34] .

Chronic intake of excessive fluoride can lead to the severe and permanent bone and joint deformations termed as skeletal fluorosis. Early symptoms include sporadic pain and stiffness of joints: a headache, stomach-ache and muscle weakness can also be warning signs. The next stage is osteosclerosis and (hardening and calcifying of the bones), and finally, the spine, major joints, muscles, and nervous system are damaged. The only remedy is prevention, by keeping fluoride intake within safe limits [35]. Research of several investigators during the last 10 years has proven that life-long 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. [36].

2.5. Distribution of fluorosis in the world and the Ethiopian context

The latest information shows that fluorosis is endemic in at least 25 countries across the globe. The total number of people affected is not known, but a conservative estimate would number in the tens of millions. In 1993, 15 of India's 32 states were identified as endemic for fluorosis. In Mexico, 5 million people (about 6% of the population) are affected by fluoride in groundwater. Fluorosis is prevalent in some parts of central and western China and caused not only by drinking fluoride in groundwater but also by breathing airborne fluoride released from the burning of fluoride-laden coal. Worldwide, such instances of industrial fluorosis are on the rise [39]

Both dental and skeletal fluorosis is prevalent in the rift valley region of Ethiopia because of high fluoride waters that originate from springs and boreholes [37]. An extensive study was done among 1,456 individuals in 14 communities in the central Rift Valley and reported dental fluorosis prevalence rates was between 69% and 98% (mean 84%) in the groups sampled. No significantly higher rates were found in young males (82.5%) as compared to young females (81%), in the age group 10-14 years. In a similar study from the Ethiopian Rift Valley, showed the prevalence of dental fluorosis in permanent anterior teeth, ranging from 34% to 75% in 8-year-old children

residing in various villages of the Wonji-Shoa Sugar Estate and 77% among adults (20-25 years old) [38].

2.6. Distribution of Fluoride in Ethiopia

Concentrations of fluoride greater than the WHO guideline value of 1.5 mg/L have been found in ground waters from several parts of Ethiopia, but are recognized to be highest in the Rift valley zone Concentrations often greater than 10 mg/L are found in waters from the Rift valley. A recent analysis of the water samples from this region (along with the roads from Addis to Hawassa and from Addis to Adama) by the Chemical Engineering Department of Addis Ababa University (AAU) shows that the fluoride concentration ranges on average from 5 to 25 mg/L [39].

2.7. Conventional methods for fluoride removal

Membrane filtration, precipitation, Nanofiltration, ion-exchange, electrocoagulation, flotation, reverse osmosis, and adsorption have been used for fluoride removal. Most of these methods have high operational and maintenance cost, low fluoride removal capacities, lack of selectivity for fluoride, undesirable effects on water quality, generation of large volumes of sludge and complicated procedures involved in the treatment. Among these methods, adsorption is the most effective and widely used method because it is universal, has a low maintenance cost, and is applicable for the removal of fluoride even at low concentrations [40].

2.7.1. Membrane filtration process

Membrane filtration processes are among advanced water treatment technologies that have been mainly employed in the treatment of pure and ultra-pure water [41]. Reverse osmosis and electrodialysis are two membrane filtration processes which can be used for removal of fluoride [42]. Reverse osmosis is an excellent choice for the reduction of fluoride [43].

2.7.2 Precipitation method

Precipitation methods based on the addition of chemicals to the water is simple and economical and is used principally for the treatment of high-fluoride containing waste water(typically greater than 10mg/L). But, the final concentration of fluoride is generally still above level prescribed by

the World Health Organization (WHO) and excess chemicals in treated water are difficult to eliminate [44].

2.7.3. Distillation method

Distillation units can be used for treating the drinking water. Large-scale electro dialysis plants are already used for making drinking water out of the brackish water with high fluoride concentrations. In many parts of North Africa, water is brackish and contains over 1.5 mg/l fluoride. Reverse osmosis and electro dialysis are advanced, large-scale treatment technologies which are difficult to use in less advanced regions [45].

2.7.4. Adsorption

Adsorption is the phenomenon of accumulation of a large number of molecular species at the surface of liquid or solid phase in comparison to the bulk. The process of adsorption arises due to the presence of unbalanced or residual forces at the surface of the liquid or solid phase. These unbalanced residual forces have a tendency to attract and retain the molecular species with which it comes in contact with the surface. Adsorption is essentially a surface phenomenon.

Adsorption is a term which is completely different from Absorption. While absorption means the uniform distribution of the substance throughout the bulk, adsorption essentially happens at the surface of the substance. When both Adsorption and Absorption processes take place simultaneously, the process is called sorption.

Adsorption process involves two components, which are adsorbent and adsorbate. The adsorbent is the substance on the surface of which adsorption takes place. Adsorbate is the substance which is being adsorbed on the surface of the adsorbent. Adsorbate gets adsorbed.

Adsorbate + Adsorbent give rise to Adsorption. For this study, the adsorbate is fluoride which can adsorb by adsorbent HA

Adsorption based processes, which involve the passage of water through a bed containing adsorbent materials to retain fluoride either by physical, chemical or ion exchange mechanisms, are very attractive due to their effectiveness, convenience, easy availability, the simplicity of operation, and economical as well as environmental low impacts. Since the past few years, adsorption is being the most interesting area in defluoridation research that is widely recognized as an ideal and appropriate compared to other defluoridation techniques, particularly for poor

communities in developing nations, although not without disadvantages because it is affected by solution pH, the presence of co-anions such as sulfate, phosphate, and bicarbonate, besides, the requirements of regeneration or an appropriate disposal of fluoride-loaded adsorbent materials[45].

2.8. Adsorbent materials for fluoride removal from aqueous solution

The starting point in the development of adsorption-based process is the choice of suitable adsorbent. Several locally available and naturally occurring adsorbent materials have been tried in the past to identify an efficient and economical defluoridating agents [46] such as the most commonly used activated alumina and activated carbon, activated clay [47], ceramic materials and bone char materials were also tried as effective and low-cost adsorbents for fluoride removal, to mention a few. A defluoridation study in Ethiopia has been started since the first recognition of the fluorosis problem in 1962 [48]. A local non-governmental organization (NGO) called Oromo Self Help Organization (OSHO) field-tested bone char technology in rural villages of Ethiopian Rift Valley [4] since 2007. Bone char is a commonly used adsorbent in developing countries for defluoridation of drinking water, mainly due to economic reasons, and has been studied by several researchers [49] However, the applicability of these methods is limited either due to their low efficiency, high production cost or lack of public acceptance in the case of bone char. Therefore, it is of paramount importance to identify adsorbent materials with a compromise between their fluoride removal capacity, social acceptance, as well as cost, in addition to technical including disposal issues for applications in rural communities in developing countries. Adsorbent materials HAp that proposed to study in this research work was expected to solve the above problems related to economic and cultural Issues.

2.8.1. Hydroxyapatite

Following human metabolism, where fluoride is removed from the water and taken up by our teeth and bones through the hydroxyapatite component, one of the most widely tested adsorbents has traditionally been hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). It is a double salt of tri-calcium phosphate and calcium hydroxide and the principal inorganic constituent of human bones and teeth. Over the past three decades, researchers have studied several aspects of the uptake of fluoride ions by tooth enamel and synthetic HAp [50].the surface of HA has a remarkable capacity for retaining fluoride ions from an aqueous solution because of the presence of exchangeable hydroxide anions. In fact,

due to the size dependent affinity of fluoride and the higher stability of fluorapatite (where hydroxide is replaced by fluoride, $Ca_5(PO_4)_3F$, Ksp= $3.16x10^{-60}$) compared to hydroxyapatite ($Ca_5(PO_4)_3OH$, Ksp= $2.34x10^{-59}$), such hydroxide anions of HAp can be exchanged by fluoride anions, resulting in a fluoride removal material . This process is governed by factors such as fluoride concentrations, calcium and phosphate ion concentration of the solution, its pH, exposure time, temperature and the nature of the apatite surface [51]. HAp has shown an excellent potential towards the retention of fluoride from water, current research is applied in an attempt to further enhance its fluoride-removal the results of which could definitely give a new dimension in the field of the defluoridation as it showed significantly higher defluoridation capacities [52].

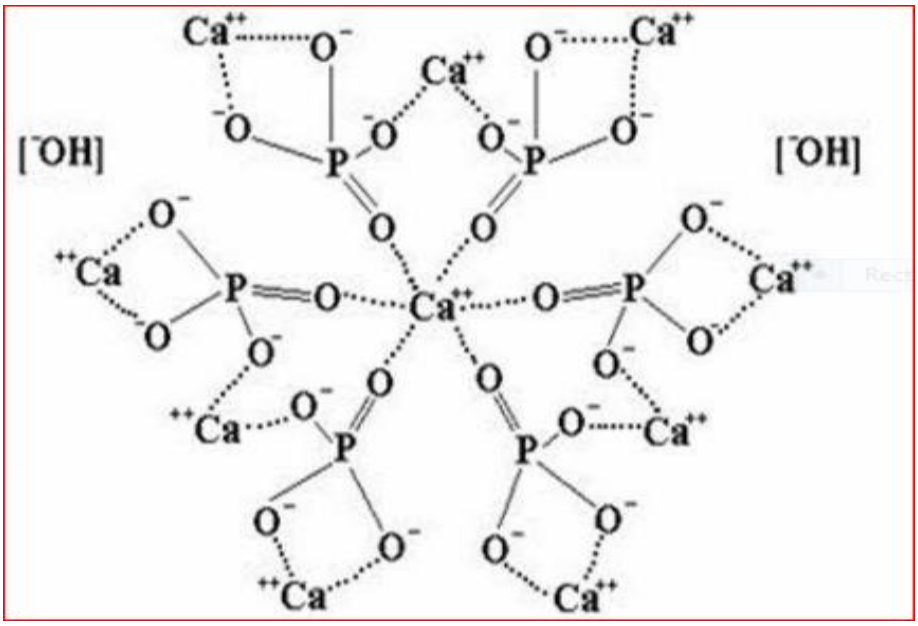

Figure 1 Crystal structure of hydroxyapatite

2.9. Synthesis methodologies of Hydroxyapatites

Due to its excellent properties and a wide range of applications, several methods of generating HA have been reported, where products are of the nano or micro-scale. A few of these techniques will be detailed in this part, including some advantages and disadvantages of each. Synthesized HA powders which are analogous to naturally occurring HA can be produced from a range of different precursors and using several different synthetic routes. A commonly used technique for manufacturing HAp are:

2.9.1. The wet chemical precipitation method

As described first by Osaka's research group [53] phosphoric acid solution will have added to calcium hydroxide in a controlled, dropwise manner with stirring. The stoichiometric ratio of calcium hydroxide to the phosphoric acid can be calculated from their balanced chemical equation .10 mole of calcium hydroxide react with 6 moles of phosphoric acid to produce one mole of hydroxyapatite and eighteen moles of water. Thus, the stoichiometric mass ratio of $Ca(OH)_2$ to Phosphoric acid should be 740 g and 588 g respectively, The reaction should conduct with various reaction temperatures between 0 and 100 ˚C with the pH monitored throughout. The study showed that higher reaction temperatures led to the formation of a more crystalline product, and processing at a pH lower than 9 led to the formation of calcium-deficient HA. This method yielded particles with a narrow size distribution; however, the lengthy time required for synthesis forms the major disadvantage of the precipitation method as both the described procedures took several days before HA powder could be obtained. In turn, this creates difficulty in producing material at commercial scale, problems with batch to batch reproducibility.

2.9.2. Sol-Gel method

This procedure essentially uses a solution ("sol"), which is left to gradually form a gel-like substance, containing a liquid and solid phase. The solvent is then removed by drying or centrifuging and decanting, to yield a powder [54] A research reported the use of the sol-gel method to produce microcrystalline HA. Here, they dissolved calcium acetate, Ca $(C_2H_3O_2)_2$, in water as the calcium source. To this, they added a triethyl phosphate solution, $(C_2H_5)_3PO_4$, dropwise until a calculated stoichiometric Ca/P ratio of 1.67 was achieved. After stirring at room temperature, the solution was left to age for 24 hours. This allowed gel formation which was then dried at 120 ˚C for 16 hours to give a powder product, which was then washed and dried again. It was found that the samples needed to be calcined at temperatures up to 700 ˚C before highly crystalline products could be obtained. The methodology is relatively simple but, again, this procedure is time-consuming, with limitations to scalability. Moreover, the calcination step can be energy intensive.

2.9.3. Hydrothermal technique

In the 20th century, the hydrothermal technique for the synthesis of materials was clearly identified as an important technology and using this technology various ceramic materials including HAp

can be synthesized. Hydrothermal synthesis is a process that utilizes single or heterogeneous phase reactions in aqueous at elevated temperature (T > 25°C) and pressure (P > 100 kPa) to crystallize ceramic materials directly from solutions [55]. However, with the hydrothermal treatment, the Ca/P ratio for the precipitates improves with the Increase in hydrothermal pressure or temperature.

2.10. Defluoridation capacities of different adsorbent

2.10.1. Defluoridation by Apatite material

The researcher has reviewed the defluoridation capabilities of calcium-containing materials. The materials for defluoridation through hydroxyapatite HA, quicklime, slack lime, calcium chloride, limestone or calcium carbonate, calcium hydroxide, calcium phosphate, calcium nitrate, calcium sulfate, bleaching powder, plaster of Paris, cement paste, hydrated cement, aluminum cement etc. Each and every mentioned above material has certain advantages and disadvantages [56].

The defluoridation process of aqueous water was carried out by the calcium-based adsorbents due to the property such, they have an excellent affinity for fluoride, low cost in nature and biocompatibility with the human body, and they make them to be used in a worldwide basis. For discussing calcium-bearing materials used as an adsorbent for removal efficiency of fluoride we have divided them as follows.

Hydroxyapatite (HA) evidently adsorbed 19 mg of fluoride per 1 g of solid at a pH range between7.0 and 7.5 [57]. The Size-dependent Defluoridation properties of synthetic hydroxyapatite from aqueous solution was observed that the HAp with smaller size particles possesses, the better fluoride removal capacity than bigger size particles. The Langmuir adsorption capacity of different size HAp ranged between 0.295 to 0.489 mg/g. The experimental data from nano-sized HAp was quite suitable with pseudo-second-order kinetics and Freundlich isotherm models and it also found that the adsorption process was basically physisorption and endothermic in nature according to the thermodynamic study. The fluoride removal efficiency increases with an increase in the adsorbent dose and contact time, but it decreases with an increase of initial fluoride concentration and pH of the solution [58].

Recent research has widely explored hydroxyapatite (HA) as an adsorbent for removal of fluoride from water. The adsorption capacity of 4.7 mg/g was obtained using 0.01 g of HAp and 25 ml of

solution and noted to be the highest value, whereas 96% of removal took place by using 0.1g of HAP and 25 ml of fluoride solution. The optimal pH range and equilibrium time were 5-7.3 and 16 hours respectively. The pseudo-second-order kinetics and Freundlich isotherm model had outstanding results from the adsorption process. The fluoride desorption was carried out by the alkaline solution of pH 10.0 [59].

Another research has indigenously employed nanostructured hydroxyapatite (n-HAp) manufactured by the combination of ultrasonic and microwave techniques during wet chemical synthesis of hydroxyapatite. The maximum adsorption capacity of 5.5 mg/g was obtained at pH 6.0 and 298K [60].

2.10.2. Defluoridation by eggshell and related materials

Eggshells mainly contain calcium carbonate (91% - 94%), calcium phosphate (1%) and other organic matters which makes it preferable for synthesizing CaO by decomposition Researcher has removed fluoride from water by using egg shell, activated carbon and rice husk ash in column study at 60 cm height of adsorbent for 10 mg/l of initial fluoride concentration. The fluoride removal efficiency of egg shell, activated carbon, rice husk ash, and mixed adsorbent was found to be 61.8%, 53.4%, 42.5%, and 62% respectively [61]. For eggshell powder as an adsorbent for defluoridation of aqueous solutions and the maximum adsorption was achieved at a pH range between 2.0 and 6.0. The fluoride removal of 94% obtained at optimal conditions such as 5 mg/L of initial fluoride concentration, 2.4 g/100 ml of dose and 120 minutes of time. The experimental data were also fitted with the Langmuir isotherm model and pseudo-second-order kinetic model. The chemisorption mechanism involved in adsorption and Intra-particle diffusion did not the sole rate controlling factor [62].

2.10.3. Defluoridation by bone char

The adsorption capacity of bone char in a column by the dynamic parameter was 3.5 and 6.6 mg/g for two different bone char materials. The results of modeling revealed that smaller grain sizes of the bone char made the fluoride sorption faster and higher hydraulic retention times or smaller flow velocities made the bone char more effective for the defluoridation [63].

The fluoride removal of 80% was achieved at pH 7.2 in a contact time of 1 hr, 15 g adsorbent dose and 5 mg/L initial fluoride concentration. The presence of anions such as chloride and sulfates had no effect on the adsorption capacity [64]. The household bone char filter performance developed by the Catholic Diocese of Nauru (CDN), Kenya in villages of Ethiopia. The fluoride removal efficiency was observed to be satisfactory and below 1.5 mg/l. The lifespan of the bone char filters was limited due to high fluoride concentration in some ground sources which was up to 23 mg/l and hence regeneration of bone char or its replacement was done frequently and in. gentle way. To overcome this limitation, CDN and Eawag developed contact precipitation method. CDN had developed pellets containing calcium and phosphate and was added to the bone char to extend the lifespan of bone char filter [4]

3. MATERIALS AND METHODS

3.1 Materials and chemicals

3.1.1. Raw materials (precursors) used for the synthesis

Fresh hen's eggshells for calcium precursor collected from Hotel and Restaurant in adama City.

3.1.2. Apparatus used for the synthesis of hydroxyapatite

Oven, furnace, magnetic stirrer, mortar, pestle, Filter paper, and Electronic mass balance. Sample holders, pH-meter, 500 ml beaker, funnel, ceramic crucible, titration setup, flasks, and measuring Cylinder.

3.1.3. Instruments

Instruments used for characterization were; TGA/DTA of a SHIMADZU DTG-60PLUS type, XRD model 7000 Diffractometer made in SHIMADZU. Spectrum 65 FTIR (PerkinElmer) Type and (FSE) Fluoride Ion Selective Electrode for defluoridation test.

3.1.4. Chemicals and reagents

Analytical grade chemicals and reagents:- H_3PO_4, NaF, NaOH, EDTA, HCl, Glacial acetic acid, Double- distilled water, Ethanol, EBT indicator, $MgCl_2$, $CaCO_3$ powder, and ammonia solution were purchased from Addis Ababa NEWAY PLC chemical shop.

3.2. Method of Synthesis of hydroxyapatite

The most popular and widely used technique for the synthesis of HAp is precipitation technique. This technique is also called as wet precipitation or chemical precipitation. Hydroxyapatite powder was synthesized from eggshell and phosphoric acid through wet Chemical precipitation. Calcium hydroxide [$Ca(OH)_2$] and orthophosphoric acid [H_3PO_4] were starting materials of this reaction. The synthesis reaction was performed using eggshell as the calcium source. In order to obtain a material with a Ca/P ratio equal to 1.67, the reagent solutions were prepared with a molar ratio of Ca/P= 0.5/0.3, i.e. 0.5 M $Ca(OH)_2$ and 0.3 M H_3PO_4. The amount of HA formed based on the amount and speed of dropping H_3PO_4 using micropipette.

The only byproduct of this reaction was water and the reaction involved no foreign elements as indicated by the following hypothetical equation.

$$10\ Ca\ (OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}\ (PO4)_6(OH)_2 + 18\ H_2O$$

As we can observe from the reaction above, the only by-product was water which implies the synthesis method is eco-friendly. The process adheres to the Principles of (Green technology) [65]. This technique is chosen to synthesize HAp in this study in contrast to other techniques. Because the relatively large amount of HAp can be produced by precipitation technique in absence of organic solvents at a reasonable cost [66].

3.2.1. Experimental procedure

Part 1

Sufficient amount of eggshells were collected from hotels and Restaurant. The surface of the eggshells was washed three times with distilled water. The internal thin layer of the shell was removed using a finger to decrease the collagens. The cleaned raw shells were boiled in distilled water for 1hr at 100 ^{0}C to remove impurities and organic matter. The eggshell was dried in an oven at 80 ^{0}C for 3 hours in order to crush and grind using pestle and mortar to obtain a powder. The eggshell residue was sieved with 150µ size sieve and calcined in a furnace at 850 ^{0}C for 2 hrs on ceramic crucible to obtain calcium oxide powder. The powder was analyzed to check the presence of calcium oxide.

Part 2

A stoichiometric amount of calcined eggshells powder (calcium oxide) was added and dispersed in distilled water in 500 ml beaker under rigorous stirring to obtain calcium hydroxide solution. Analytical grade phosphoric acid was diluted to 0.3 M and added dropwise into the suspension at room temperature by monitoring the pH with pH-meter until the pH reaches 8.5. The solution was subjected to aging treatment for 12 hr. followed by stirring on a magnetic stirrer for 30 minutes without heating and left for extra 10 hr for precipitate formation. The precipitate was washed and filtered using a Whitman No. 1 filter paper. Finally, the precipitate was dried in an oven by 80 ^{0} C for 3 hr. and calcined at 900 ^{0} C in a furnace on ceramic crucible for 2 hr to obtain the powder [66].

3.3. Characterization

In this study characterization of the synthesized powder was accomplished by TGA/DTA, XRD, and FTIR. TGA/DTA was used for thermal analysis before and after calcination to obtain the mass loss during the experiment. The mass loss is automatic because of the evaporation of water. XRD use to estimate the crystal structure and crystal size. FTIR also use to identify functional group percent in synthesized hydroxyapatite powder. The instruments are listed below with their specification and working principles.

3.3.1. TGA (Thermogravimetric) analysis

TGA is used to study the change in mass of a sample as the temperature is varied. By controlling the atmosphere e.g. with O_2 or N_2, it may be possible to encourage or suppress oxidation reactions, thus controlling to some extent the nature of the thermal events occurring [67]. When heated to 1000°C, many materials undergo weight changes giving characteristic curves. Where the changes can be linked to the particular thermal events, such as oxidation, or loss of water of crystallization, the size of the step in the curve can be used for the quantitative analysis. For this particular work, we used TGA analysis for the determination of the calcination temperatures using a SHIMADZU DTG-60PLUS instrument.

3.3.2. XRD analysis

X-ray diffraction (XRD) is a versatile, non-destructive instrument that is used for the determination of atomic arrangement within a material, giving the crystalline phases from the atomic spacing and symmetry. In this technique, X-rays of a known wavelength are passed through a sample to fully investigate its crystalline structure. The wave nature of the X-rays means that the lattice of the crystal gives a unique diffraction, which results in a pattern of peaks of ‘reflections’ at varying angles and with different intensities. The diffracted beams from atoms in successive planes cancel unless they are in phase, and the condition for this is given by the Bragg’s law [68]:

$$\lambda = 2dSin\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (Bragg' \text{ Law}).$$

Where; λ is the wavelength of the X-rays, d is the distance between the different plane of atoms in the crystal lattice and θ is the angle of diffraction. Prior to XRD analysis, the samples were ground

using a marble mortar and pestle before distributing 100mg of the ground sample powder over a 10mm diameter. The prepared HA samples were analyzed by XRD using a high resolution with a CuKα monochromatic beam (wavelength=0.154056 nm) produced at 40 kV and 30 mA. XRD spectrum was recorded from 10^0 to 80^0 with 2θ angles.

Phase Identification

For the phase identification step, the X-ray diffraction patterns were directly compared to the files for HA from the Joint Committee for Powder Diffraction Standards (JCPDS, Card No. 09- 432) as was supplied by the International Centre for Diffraction Data (ICDD).

Crystal size

The crystal size, of the precipitates, was estimated from XRD pattern using the Scherer's formula [69]. According to this equation, a single crystal dimension perpendicular to the (h k l) plane (D h k l) (nm) can be estimated from the peak broadening

$$D = \frac{k\alpha}{FWHM} C \text{----------equ-(3.1)} \quad (Scherrer's formula)$$

Where D is the crystal size in nm; K is the Scherer constant (0.9 for hexagonal HA), α is the wavelength of the monochromatic X-ray beam (0.15418 nm); FWHM is the experimental Full Width at Half Maximum intensity of the diffraction peak under the consideration peak; θ is the diffraction angle (°). In samples with apatite structures, the line broadening of the (002) reflection was used to evaluate the mean crystal size, which corresponds to the c crystallographic axis.

3.3.3. FTIR- (Fourier Transform Infrared) spectroscopy

Fourier transform infrared spectroscopy (FT-IR) is a chemical analysis technique that generates a molecular fingerprint of the samples. It is based on the vibrations of the atoms, which are subjected to a passing infrared radiation and measures the ratio of the incident radiation absorbed at a particular energy when the sample is exposed to different wavelengths of infrared light, transitions between vibrational energy levels of various chemical bonds are detected, allowing for the functional groups within the molecules of the sample to be identified. The resulting spectra, which are a characteristic of infrared absorption/emission at different wavelength, can be used to define the chemical composition of the sample. In this study, FT-IR was used for further confirmation of

the chemical composition of the samples. FT-IR spectroscopy was handled by Spectrum 65 FTIR (PerkinElmer).

3.4. Sample preparation of synthesized powder for characterization

Sample preparation for TGA/DTA analysis

The synthesized powder was sieved with 50 μ size sieve and 1omg of the sample was weighed on electronic mass balance then it was placed in the alumina crucible by TGA/DTA instrument and analyzed under air atmosphere with heating rate of 10°C/minute.

The sample for XRD analysis

Prior to XRD analysis, the samples were grained using a marble mortar and pestle before distributing 100mg of the ground sample powder sieved by 50μ size sieve to obtain the a10mm diameter circular area of 20mm. The prepared HA samples were analyzed by XRD using a high Resolution with Cu Kα monochromatic beam (wavelength=0.154056 nm) produced at 40 kV and 30 mA.

The sample for FTIR analysis

Sample preparation was done by mixing 2mg of each sample with 300mg of Potassium bromide (KBr), compressed to form a pellet and then placed on specimen holder from 400 to 4000cm^{-1}.

3.5. Sample preparation of synthesized HAp for defluoridation test

After characterization of the Synthesized HA, four Samples of the powder accurately weight on electronic mass balance for defluoridation test. The samples have a constant interval, 1g, 3 g, 5 g, and 7g.

3.6. Preparation of stock solution for defluoridation test

A stock solution of fluoride was first prepared by dissolving 2.21 g of sodium fluoride in 1000ml distilled water in a plastic flask. Equal intervals of fluoride solution 5, 10, 15 and 20 mg/L fluoride were prepared by serial dilution from the stock solution for defluoridation test.

3.7. Preparation of raw water sample for defluoridation test

Six equal Sample size (30 ml) of groundwater real Samples (raw water) were donated from Bofo and Security sites under the supervision of OSHO Lab Technical for the practical defluoridation test. Three samples from Bofo Located at East Shewa Lome district and three from Serenity East Shew around Meki Town. The samples were carefully measured with the granulated cylinder and kept in a 50ml plastic beaker until their fluoride concentration are determined by Fluoride selective Electrode (performed Lab Analyst). The row Water samples fluoride concentration were 8.3 and 10.5 mg/L fluoride respectively and both are above the WHO Guideline. The defluoridation test was done with 1g, 3g and 5g doses of synthesized HA powder by using the same procedure for optimizations.

3.8. Preparation of TISAB (Total Ionic Strength Adjustment Buffer)

500ml of double distilled water, 7g $Na_2C_6H_2O_7$, 56gSodium Chloride, and 2 g EDTA are added into a 1000ml beaker and then Stirred to dissolve. After the solution was dissolved, 57g of glacial acetic acid is added into it and finally, 5M Sodium hydroxide was added until the pH reached 5.3, then transferred to a 1000mL volumetric flask and double distilled water is added to mark.

3.9. Calibration of the electrode

20ml of fluoride Solution with different fluoride ion concentrations were prepared in constant intervals and 2 mL of TISAB was added to each solution. The potential (E in mv) verse the Logarithm of concentration (Log c) in mg/L was drowned. The Slope of the graph and R^2 were Calculated to check the accuracy of the measurement. The prepared concentration of fluoride 2.5, 5, 7.5 and 10 mg/L was used for calibration.

3.10. Fluoride determination technique.

Fluoride ion concentration was determined by fluoride ion Selective Electrode. For this study, the HAp powders were separately added on to 30 ml of known concentration of fluoride water 5mg/L 10mg/L 15mg/ L and 20 mg/L fluoride in 50 ml plastic beaker. 2ml of Total ionic strength adjustment buffer (TISAB) solution prepared with the 10.1 volumetric ratios was added in order to maintain ionic strength and the pH and to eliminate the interference effect of complex ions in

the solution. In this way, the Effect of different parameters like contact time, pH, adsorbent dose and initial fluoride concentration was obtained by varying one parameter and other parameters constant. Finally, the Equilibrium Fluoride Concentration (Residual) for each test were determined using a pH /ISE meter with combination to Fluoride Selective electrode. The pH was measured with a pH /ion meter The Electrode were Calibrated prior to each experiment.

3.11. Measurement with electrode

The electrodes were immersed in to the sample solution & measure the developed potential while stirring on a magnetic stirrer.Let the electrodes remain in solution until the millivolt reading was constant or no drift sign visible on the screen of the electrode. The electrodes with drawled and rinsed with distilled water and blotted dry between readings (blotting may poise electrode if not done gently). Measurement of a standard sample made repeated & recalibrated or measured a standard fluoride solution after measuring 4-8 samples.

3.12. Defluoridation test

For this study, all experiments were conducted using 30ml of 10 mg/L of fluoride solution taken in four different 50 ml plastic beaker. 1g, 3g, 5g and 7g HAP samples were added in this solution for different contact time. Then, the solution stirred at room temperature for 1minut to achieve equilibrium on a homogenous solution. Each sample was periodically taken and filtered on their contact time 1hr, 3hr, 5hr, 7hr, 11hr, and 24 hr. with a Whitman No. 1 filter paper before fluoride analysis. The fluoride selective electrode reads the electro volt intermesh of a millivolt. The millivolt was converted into mg/L of residual fluoride concentration using pre-determined Calibration slop by Microsoft Excel. The adsorption efficiency (%) and the defluoridation capacity (mg F- adsorbed/g of adsorbent) at a given contact time for the selected adsorbents were determined using the Equation (.3.2.) and (3.3) [70].

Percentage removal $= \frac{[Co - c_t] \text{x } 100}{Co}$ ----------equ (3.2)

Adsorption capacity= $\frac{[Co - c_t]\, x\, V}{m}$ ----------equ (3.3)

Where C_0 is initial fluoride concentration, C_t is resthe idual fluoride concentration at time t, m is mass of the adsorbent, and V is volthe ume of the solution used in the batch.

3.13. Optimization of different parameters

Optimization is carried out to make some parameters function at their best by varying one parameter while keeping other parameters constant in this study the effect of major parameters like adsorbent dose, contact time, initial fluoride concentration and pH were optimized to investigate the Maximum Defluoridation Efficiency of the Synthesized HAP from hen's eggshell in this work assigned as natural hydroxyapatite (nHAp).

3.13.1. Effect of adsorbent dosage

Experimental investigations were carried at different dosages of adsorbent 1g, 3g, 5g and, 7g in 10 mg/L of fluofluoride initial concentration at 5 hr contact times and pH three.

3.13.2. Effect of contact time

Residual F^- concentrations were measured for different contact time of adsorption,1, 3, 5, 7, 11 and 24 hours with 5 g of adsorbent (HAp) in order to investigate the effect of contact time. Other parameters like pH, concentration of the solution and HA dosage remain constant [70]. In this section the kinetics of the adsorption data was analyzed based on reaction kinetics of pseudo-first order and pseudo- second-order mechanisms

3.13.3 Effect of Initial Fluoride Concentration

To investigate the effect of initial fluoride concentration experiments were conducted at various fluoride concentrations (5, 10, 15, and 20 mg/L) keeping pH=3 and temperature constant with fixed 5 g of adsorbent and 5 hr. contact time .

3.13.4. Effect of pH

To study the effect of solution pH on fluoride removal, the test solutions containing the optimized concentration of fluoride were adjusted to pH values of 3, 5, 7, and 9 using 1N HCl and 1N NaOH and the adsorbent was remain constant through acidic, neutral and basic media. Then, the determined does 5g HAp was added in into each test solutions separately and stirred for 1 to reach

equilibrium. Residual fluoride ion concentrations were analyzed in each experiment after5 hr. contact time. Finally, pH versus percentage removal graph was plotted to describe the adsorption behavior of the adsorbent HAp at each pH.

3.14. Adsorption isotherm models

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species between liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity or homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species [71]. The relationship between the amount the substances sorbed at constant temperature and its concentration equilibrium solution called adsorption isotherm. The equilibrium adsorption isotherms are of fundamental importance in the study of adsorption systems. The two well-known adsorption isotherm models for surface coverage studies are Langmuir and Freundlich isotherm mode.

3.14.1. Langmuir adsorption isotherm

The Langmuir isotherm model is most commonly used to quantify the amount of adsorbed on an adsorbent as a function of concentration at a given temperature. Langmuir isotherm assumptions:

1. Intermolecular forces decrease rapidly with increase of and distance consequently predict the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent.

2. Adsorption occurs at specific homogeneous sites within the adsorbent.

3. Once adsorb ate molecule or ion occupies active sites, no further adsorption can take at that site.

4. All adsorption sites are identical and energetically equivalent.

Theoretically, the adsorbent has a finite number of sites for the adsorb ate. Therefore, saturation value is reached beyond where no further adsorption can occur. Linear forms of the Langmuir.

$$\frac{Ce}{qe} = \frac{Ce}{qe} + \frac{1}{b}Qe \quad \text{..... (equ. 3.4).}$$

Where,Qe is the amount of fluoride adsorbed per unit mass of adsorbent (mg/g), Ce is the equilibrium concentration of the adsorbate (mg/L), Qe and b represent maximum adsorption capacity and energy of adsorption, respectively. Langmuir parameters Qe, and b are determined from the slope and intercept of the linear plot Ce/QE versus Ce respectively. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless separation factor or equilibrium parameter, R_L which is defined by:

$$RL = \frac{1}{1+Cob} \text{.....(equ 3.5).}$$

where, Co s the initinitial concentrationthe the adsorbatetin thetion, b is is themuir's adsoadsorption constantg). The The valueR_L indicates the the typeisotisotherm toeither favorable ($0<R_L< 1$), unfavorable ($R_L>1$) or irreversible ($R_L = 0$) [72].

3.14.2. Freundlich adsorption isotherm

The Freundlich isotherm equation takes in to account repulsive interactions between adsorbed solute particles and also account for surface heterogeneities. The equation is adequate to describe non - linear adsorption in narrow range of adsorbate concentration. The logarithm form of the Freundlich isotherm is given as follows.

$$\text{Logqe} = \frac{1}{n}\log Ce + \text{logkf} \text{..... (equ. 3.6)}$$

Where, q_e is the amount of fluoride ion adsorbed at equilibrium. Ce is the concentration of fluoride solution at equilibrium; K_f and are equilibrium constant indicates adsorption capacity of the adsorbent and adsorption intensity respectively.

Finally the applicability of two adsorption isotherm (Langmuir and Freundlich) can be compared by evaluating the multiple regression correlation coefficients, R^2 In regression, the R^2 coefficient of determination is a statistical measure of how well the regression line approximates the real data points was demonstrated in Table 4.

3.15. pH at potential of zero charge (pH_{zpc}) determination

It is well known that the study of adsorption from solution strongly demands the knowledge of the point of zero charge (PZC), because the ability of the adsorbent materials to adsorb, either anions or cations, is defined by the charge on the adsorbent surface The Isoelectric point or Zero point charge (pH_{zpc}) of the carbon samples were measured by using the method described by [73]. 0.1 M of 10 NaCl solutions having the initial pH values ranging from 2 to 11 with 1 increment were prepared in duplicate using 0.1 M HCl and 0.1 M NaOH. While in one each duplicate 2g of HAp was added and mixed for 0.5hr. Then the solutions were filtered off and the adsorbent was separated. The final pH values of the ten solutions were measured by PH-meter and thereby calculation of ΔpH was made by subtracting the initial pH values from final pH values. The graph was drawn by plotting the final pH values against ΔpH. From the graphs plotted, the pH_{zpc} (point of zero charge) of the adsorbent was determined.

3.16. Kinetic of adsorption

It is very important to know the rate at which the adsorption process takes place and the factors that control the rate of the process, for this purpose, kinetics of the process were evaluated The study of adsorption kinetics describes the rate of uptake of the adsorbate molecule , in this case fluoride ion onto adsorbent, which determines the residence time required for design adsorption systems. This rate depends on the physic- chemical characteristics of the adsorbate and adsorbent, pH of the solution, temperature, and concentration of the solution. The adsorption kinetics shows the evaluation of the adsorption capacity though time and it is necessary to identify the adsorption mechanism in a given system. The following models are used to describe the adsorption kinetics behavior.

3.16.1. Pseudo-first- order equation

The adsorption kinetic describe by the Lagergren pseudo- first - order equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expressed as follows [74].

$$\frac{dq}{dt} = k1(qe-qt) \text{----------(equ3.7)}$$

Where, qe and qt refers to the amount of fluoride ion adsorbed per unit mass of the adsorbate at equilibrium time and any time, (mg/g), respectively and K1 is the rate constant of

pseudo first -order adsorption Integrating Equation (3.7) by applying the boundary conditions qe=0 at t=o and qt=q to obtain the following linear equation t at t=t gives

$\frac{logqe}{qe-qt} = \frac{k1t}{2.303}$…….. (equ 3. 8).

Equation (3.8) can be rearranged to obtain the following linear equation form and it can be described by ln:

ln qe-qt=ln qe- k1t……..(.equ 3.9)

The rate constant, K1 and equilibrium adsorption capacity, q e can be predicted from the slope and intercept of the linear plots of log (q e - qt) versus t, respectively.

3.16.2. Pseudo- second- order equation

The adsorption kinetics may also be described by the pseudo- second- order equation. The rate of pseudo- second- order equation is dependent on the amount of solute adsorbed on the surface of adsorbent and the amount of adsorbed at equilibrium. The differential equation is given as follows [74].

$\frac{dqt}{dt}$ $K^2 (q e –q t)^2$…… (eqn.3.10).

Where, K_2 is the rate constant of the pseudo - second –order equation (g/mg min.) and qe is equilibrium adsorption capacity (mg/g). Integrating Equation (3.10) by applying the boundary conditions q_t =0 at t =0 and qt =qt at t = t is simplified and rearranged to obtain linearized equation:

$\frac{t}{qt} = \frac{t}{qt} + \frac{1}{k2qe2}$…… (equ 3.11).

The values of q_t and K^2 can be determined experimentally from the slope and intercept of the plots of t/qt versus t, respectively.

3.17. Data analysis technique

After the characterization of the Synthesized HAP Samples, the defluoridation capacity of the synthesized HAP was tested on the laboratory prepared fluoride solution and raw water samples were taken from Bofo and Serity site in Modjo Fluoride Mitigation center. Then, all the Data were analyzed and interpreted for Fluoride removal efficiency was done using Microsoft excel and Origen8 for XRD, FT-IR, and TGA/DTA. The result was compared with others pervious literature result. Finally, conclusion and recommendation were given in the thesis.

4. RESULT AND DISCUSSION

4.1. Characterization of the Calcium precursor material (eggshell powder)

4.1.1. TGA/DTA result of eggshell powder

The calcium precursor used for the HA synthesis was derived from the decomposition of eggshell. The complete calcium precursor decomposition temperature was obtained from TGA/DTA result. The Thermogravimetric analysis (TGA) of the eggshell powder was carried out between the room temperature and 1000°C in order to determine the thermal stability and the decomposition temperature of eggshell powder. The TGA result revealed that a significant mass loose was observed between the temperatures 600-800°C probably, due to the removal of impurities and the eggshell residue was stable above 800°C as indicated on figure 2.

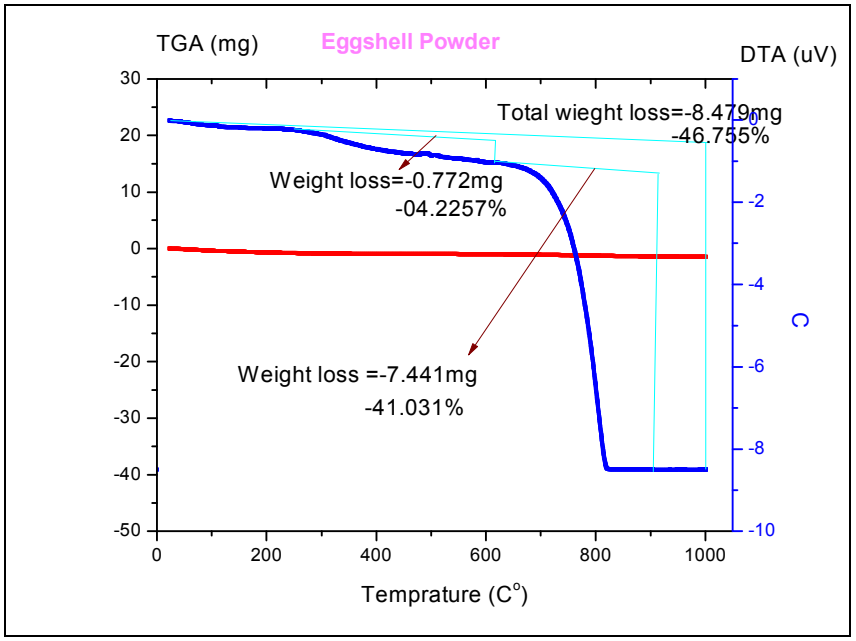

Figure 2 TGA/DTA result of eggshell powder

4.1.2. XRD result of calcined eggshell

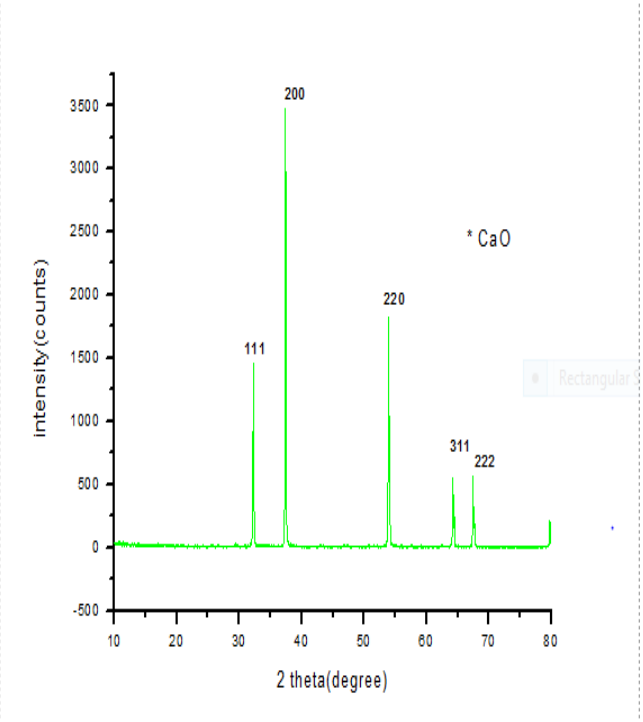

Figure 3. XRD pattern of calcineted eggshell at 850ºC.

XRD diffraction graph of calcined eggshell residue at 850°C is shown in Figure 3. The diffraction peaks at the position of 34.078°, 37.123°, 54.351° and 63.613° corresponded to (111), (200), (220) and (311) planes shown on the graph are in good agreement with the standard JCPDS file (JCPDS-82-1691) for CaO [75].

4.2. TGA /DTA result of uncalcineted HA.

In order to determine the calcination temperature for the formation of pure phase hydroxyapatite crystal, TGA/DTA experiments were done on the powder synthesized from calcined eggshell residue

at 850°C and phosphoric acid. As illustrated on figure 4. The result revealed that materials is stable or has no significant mass loss above 900°C.

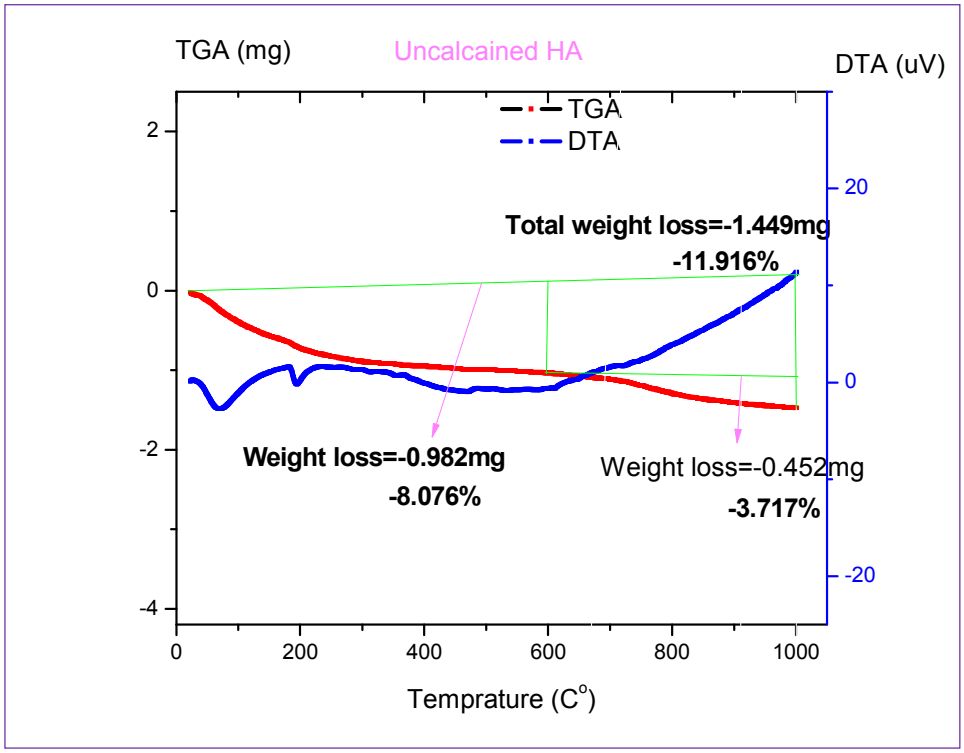

Figure 4: TGA /DTA pattern for the synthesized

4.3. XRD result of HA powder

The XRD pattern of HAp obtained after calcination at 900 °C is shown in Fig.5. According to this figure, there is no peak attributable to possible impurities, which indicates the final product is highly pure HA according to ICDD powder diffraction file (pdf) number 009-0432. All possible peaks can be indexed to the pure hexagonal phase of HAp (P63mc) without secondary phases such as α-TCP and β-TCP. This confirmed the successful synthesis of pure phase HA via the chemical precipitation from calcined eggshell residue.

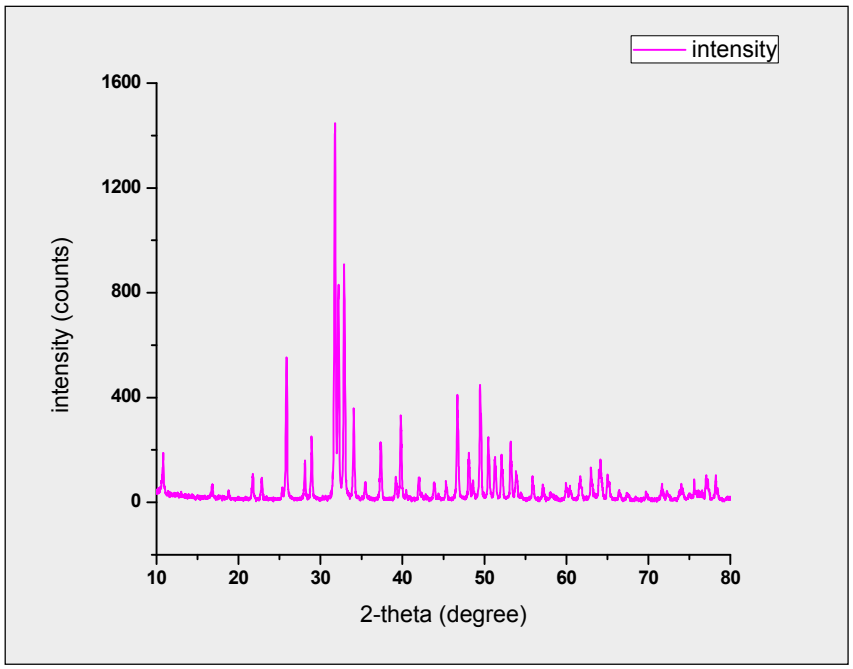

Figure 5 XRD pattern of HA powder calcined at 900ºC.

The crystal size of synthesized HA.

The crystal size was estimated from the XRD pattern using the Scherer's formula. According to this equation, a single crystal size and an average crystal size can be obtained, Where D is the crystal size in nm; K is the Scherer constant (0.94 for hexagonal HA), ⅄ is the wavelength of the monochromatic X-ray beam (1.54 nm).

$$D = \frac{k\lambda}{\beta cos\theta} \quad , \qquad D_1 = \frac{k\lambda}{\beta cos\theta} = \frac{0.1448164}{0.00286701206} = 50.5 \text{ nm.}$$

$$D_2 = \frac{k\lambda}{\beta cos\theta} = \frac{0.1448164}{0.00320552345} = 45.20 \text{ nm}$$

$$D_3 = \frac{k\lambda}{\beta cos\theta} = \frac{0.1448164}{0.002974006\ .} = 48.7 \text{ nm}$$

$$D_{AV} = \frac{k\lambda}{\beta cos\theta} = \frac{D1 + D2 + D3}{3.} = \frac{50.5+45.2+48.7}{3.} = 48.13 \text{ nm}$$

4.4. FT-IR result of calcineted HA

The graph shows broad bands around 2335 cm^{-1} and 3444 cm^{-1} of the OH- bond stretching [76]. The major peak of phosphate group, vibration peak could be identified in the region between 1414 and 1040 cm^{-1}, which is the most intensified peak among the phosphate vibration modes. The band at 595 cm^{-1} belong to vibration mode of phosphate group which occupies two sites in the crystal lattice [66].

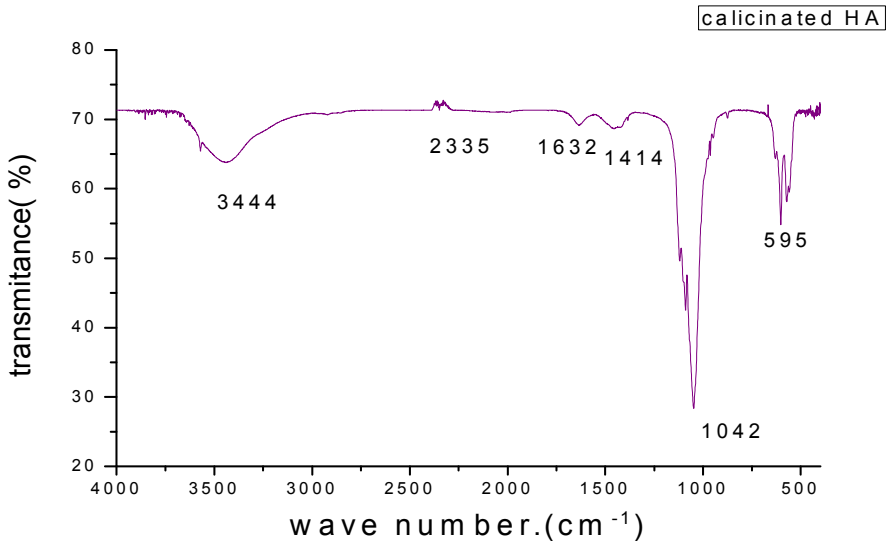

Figure 6 FT-IR patterns of Calcinated HA Powder.

4.5. Application of HAp on prepared fluoride Solution.

4.5.1. Determination of adsorbent dose (HA)

Experimental investigations were carried at different dosages of adsorbent 1g 3g, 5g, and 7g in 10mg/L of initial fluoride concentration at 5hr contact times and pH=3. The concentration range was selected based on the preliminary optimization test results at room temperature. As described in Figure 7, the fluoride removal efficiency notably increases with increasing adsorbent dose up to 5g due to the availability of more number of fluoride binding sites. As identified, the equilibrium was fully established at 5g dose with high fluoride removal of about 99%. When the initial fluoride

Concentration is 10mg/the equilibrium fluoride concentration falls within the WHO limit and no significant change on the efficiency beyond this 5g adsorbent dose. Therefore, 5g was considered as an optimum dose for further adsorption experiments. The adsorption verses percentage removal of fluoride was given in Figure 8.

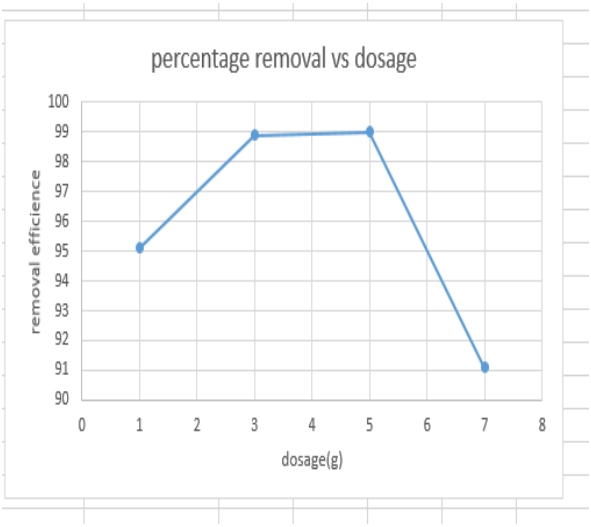

Figure 7 Investigation of the optimum dose test using 10mg/L initial fluoride concentration, pH 3 and contact time 5 hr.

The experimental result of different HA dose exhibited decreased adsorption capacity and increased adsorption efficiency with increased adsorbent dosage (Fig.7). It seems that increasing of fluoride removal efficiency with an increase in adsorbent dosage was due to the increased in the availability of fluoride-binding sites. The decrease in capacity is due to the depletion of fluoride in the solution with increasing dose of adsorbent.

4.5.2. Determination of contact time.

In order to identify the effect of contact time on adsorption of fluoride on hydroxyapatite batch experiments were carried with different contact times (1hr, 3 hr, 5hr, 7hr, 9hr, and 11 hr) fixed (dosage 5g, 10 g/L fluoride concentration pH = 3 and room temperature reaction conditions). As shown in figure 9 rapid fluoride removal was observed at the initial stage until reach to equilibrium time (5 hours) with a high removal efficiency of about 99 %. This is due to a high number of active site at initial stage leads to high diffusion of fluoride towards the adsorbent surface. As shown in figure 8, after equilibrium time slowly desorbed from the surface of adsorbent to the solution.

Therefore, this parameter determines the rate of mass transfer from the solution to the surface of the adsorbent and the data were used to study the kinetics study of batch adsorption. This trend was also reported by other studies on defluoridation processes. This is due to faster saturation of the active sites with time. This implies that the adsorbent has a specific number of active sites, which eventually are saturated after prolonged exposure to fluoride solution. After saturation of the active sites, no further adsorption is carried out on the Residual Fluoride Concentration

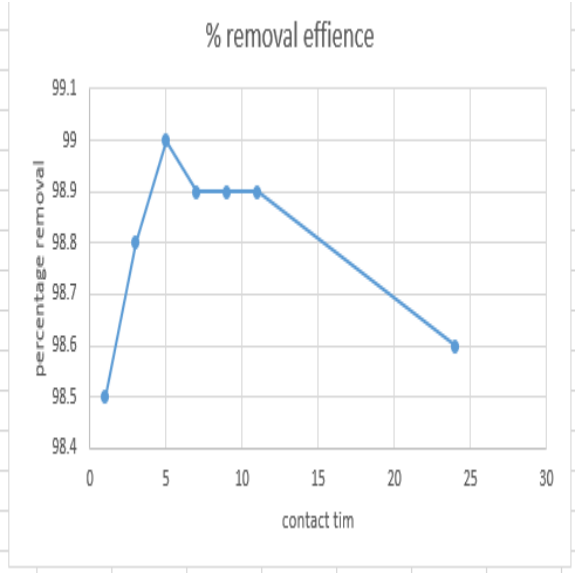

Figure 8: Fluoride removal efficiency as a function of contact time at 5 g of HAp dose, pH = 3 and initial concentration of 10 mg/L.

4.5.3. Determination of initial fluoride concentration.

For this test, the initial concentration selected randomly with 5 increments from 5-20 mg/L. The effects of other parameter remain constant and the adsorbent dose was 5 g with 30 mL solution [77]. The initial fluoride concentration showed influence on the removal capacity of the adsorbent.

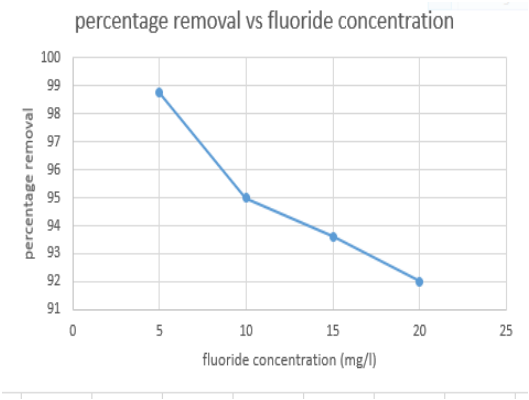

Figure 9: The effect of initial fluoride concentration on percentage removal of fluoride using 5 g adsorbent, 5 hr. contact time and pH =3.

For given mass of adsorbent, the fluoride removal capacity increase with increasing initial concentration. The increase in adsorption capacity with an increase in initial fluoride concentration is due to increased diffusion of fluoride to adsorption sites and utilization of less accessible or less active sites of the adsorbent. In this case, the optimized result is selected as 10 mg/L which is encountered 95% removal efficiency and the residual fluoride concentration were 0.5 which satisfied the optimum WHO guideline for drinking water. Higher percentage removal efficiencies at lower initial fluoride concentrations were due to a higher ratio of active surface area to total fluoride ions, which leads to the utilization of more accessible energetically active sites on the adsorbent surface. The reason for the sharp decrease of percent removal efficiency with the increase in initial fluoride concentration is lack of sufficient surface area to accommodate more fluoride ions available in the solution [78].

4.5.4. The effect of pH on percentage removal of fluoride.

The pH of the adsorbate solution is an important controlling parameter in the adsorption process. To make inclusive all the 3 media, the pH range was deliberately selected from 3-9. The effect of pH of the fluoride ion removal was studied by varying the pH from 3 to 9 with 2 increments. As illustrated in figure 4.10.

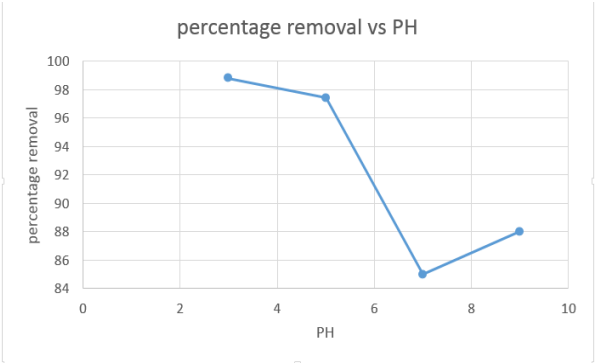

Figure 10: The effect of pH on the percentage removal of fluoride at 5g adsorbent pH=3 and 5 hr.

It was observed that the maximum removal efficiency was achieved at pH 3 which is 98.8%. When the pH increases, a decrease in the fluoride removal extent of adsorbent was observed. The main reason behind for better adsorption at low pH values may be because of the presence large number of H^+ ions at these pH values. This leads to neutralization of the negatively charged OH^- ions on the adsorbed surface and hence reducing hindrance to the diffusion of fluoride ions. At higher pH values, the reduction in adsorption may be possible due to the abundance of OH^- ions causing increased hindrance to diffusion of fluoride ions. It was observed that the surface adsorbed anions favorably in low pH range due to the presence of H^+ ions, whereas the surface was active for the adsorption of cations at high pH values due to the accumulation of OH^- ions [79]. Therefore, pH is determinant to drinking water and hence, the optimum removal efficiency for this adsorbent HA was 85% observed on pH= 7.

4.6. Application of HAp on raw water defluoridation test

samples of water were collected from two different locations of Oromia region East Showa district, near to Adama city 1, from Bofo around Bati Lome District and 2, from around Maki Town, Security groundwater with fluoride ion concentration of 8.3 mg/L and, 10.5mg/L respectively, which is still more than permissible limit of WHO. After adsorption the fluoride ion concentration of the two samples were measured and it was found that the fluoride ion concentration was decreased significantly in both adsorbent dose 1g,3g and 5g, at temperature of 25 C, rotation speed of 400rpm for 1 minute steering time, 5h contact time and at optimum pH =7 adjusted by drop of 1M NaOH. The HA adsorbent almost had good removal efficiency for field samples on the comparable condition to the result obtained on fluoride

solution test. In this paper, it was observed that on the two sites the synthesized HA material shows fluoride removal efficiency of 81.92 and 82. 85 % respectively for Bofo and Serity upon adding of 5g dose and at pH 7. The final pH of the treated water was found in the range of 7.5 to 8.

4.7. Experimental result on adsorption isotherm

Although there are different adsorption isotherm models, the two most frequently used models, Langmuir and Freundlich, have been applied as they give a good description of experimental behavior in a large range of operating conditions. For this study, the data based on the optimized fluoride concentration were interpreted in Table 1

Table 1. Langmuir's Adsorption Isotherm data for concentration verses adsorption capacity

Co,mg/L	Ce	Qe	Log Ce	Log Qe	Ce/Qe
5	0.25	0.0285	-0.6020	-1.5451	8.7719
10	0.50	0.0570	-0.3010	-1.2441	8.7719
15	0.96	0.0842	-0.0177	-1.0746	11.4014
20	1.6	0.1104	-0.2041	-0.9570	14.4927

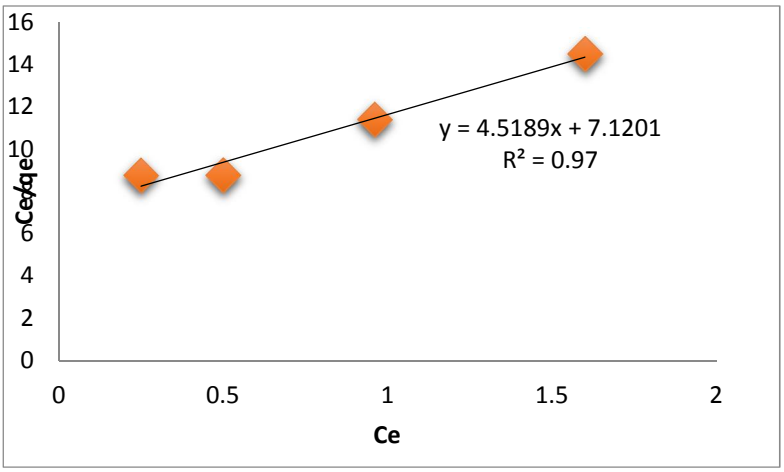

Figure 11: Linearized Langmuir adsorption Isotherm for Fluoride adsorption.

As it can be observed from the $R^2 = 0.97$ is less than one and hence, the adsorption fever Langmuir adsorption Isotherm model.

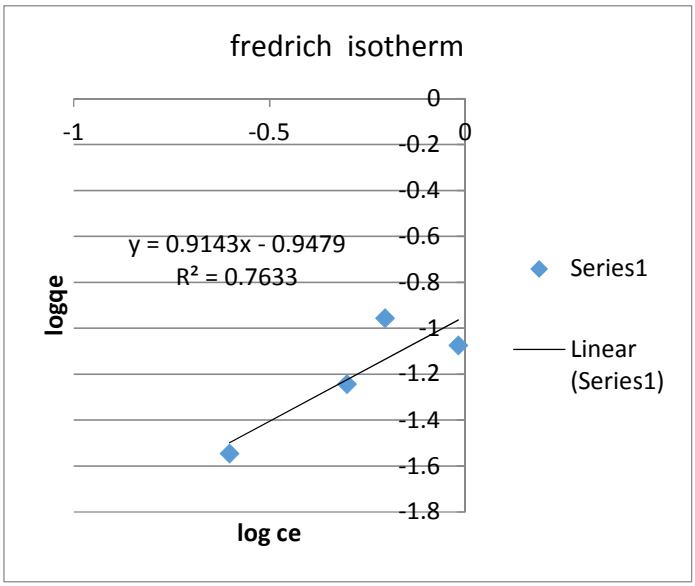

Figure 12 Freundlich isotherm graph of adsorption fluoride by HA

Table 2. Langmuir and Freundlich isotherm model parameters describing the HAp Fluoride adsorption at constant adsorbent dose 5 g, contact time 5 hr. and pH =3

Parameter	Langmuir model	Parameter	Freundlich model
Q mg/g	0.2212	KF	0.3879
b L/mg	0.6349	1/n	0.914
R^2	0.9657	R^2	0.763

Table 3. Dimension Less separation factors (R_L)

Concentration (mg/l)	5	10	15	20
R_L	0.235	0.136	0.095	0.073

To determine whether the adsorption favors' Langmuir or Freundlich model we can apply the comparison of R^2 or R_L favored Langmuir's ($0<R_L< 1$), unfavorable ($R_L>1$) or irreversible ($R_L = 0$) [56]. Therefore, as we can observe from the R^2 value, 0.96 which is less than one the adsorption isothermal obeys the Langmuir's model. The value of correlation coefficients, ($R^2 = 0.9657$) for Langmuir isotherm is higher in comparison to that obtained for Freundlich isotherm. For the Freundlich model, the value of correlation coefficient (R^2) was 0.763. The maximum adsorption capacity of the adsorbent for Langmuir isotherm is greater than for the Freundlich model. Hence, it can be concluded that the Langmuir isotherm model is more suitable for adsorption of fluoride ion than Freundlich isotherm on the basis of the experimental study.

4.8. Adsorption kinetics models

The kinetics of adsorption describes the solute uptake rate, which in turn governs the residence time of the sorption reaction. The pseudo-first-order and pseudo-second-order kinetic models were used to investigate the adsorption kinetics of fluoride and to quantify the extent of uptake in the adsorption process. It is one of the important characteristics in defining the efficiency of sorption. In the present study, the kinetics of fluoride ion removal was carried out to understand the behavior of the synthesized hydroxyapatite.

4.8.1. Pseudo first-order kinetics model

The pseudo-first order kinetic model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. The values of log ($q_e - q_t$) were linearly correlated with t. The values of K_1 and q_e were calculated from the slopes and intercepts of log (qe – qt) against the t plots using equations (4.5) and the different parameters of pseudo first and order kinetics are given in Table 4

$$\text{Log } (q_e - q_t) = \log (q_e) - \frac{K_1}{2.303} t \quad \text{.....equ (4.1)}$$

Table 4. Kinetic data obtained by varying contact time using constant adsorbent dose 5g, HA, PH =3 and 10 mg/g of fluoride concentration.

Time hr.	Residual fluoride	Qt(mg/g)	t/Qt	Ln(Qe-Qt)	LnQt
1	0.15	0.0591	16.92047	-8.1117	-2.82855
3	0.12	0.0592	58.67567	-8.5171	-2.8265
5	0.10	0.0594	84.17508	∞	-2.8234
7	0.11	0.0593	118.04384	-9.2103	-2.8251
9	0.11	0.0592	151.77065	-9.2103	-1.8251
11	0.13	0.0592	185.81081	-8.5171	-2.8268
24	0.13	0.0592	405.40545	-8.5171	-2.8268

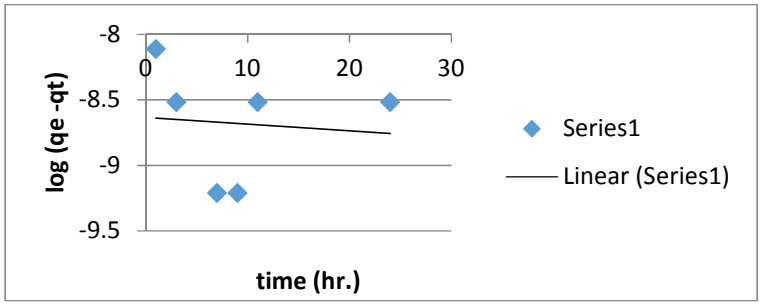

Figure 13 Pseudo First Order Kinetic result.

Table 5.adsorption kinetics parameter for pseudo first order

Pseudo First order Kinetics	Intercept	K_1	R^2	Q_e
	-8.634	0.005	0.0089	-0.1602

For kinetic studies, 5g of HAp would be contacted with 3omL of fluoride solution having fluoride concentration of 10, at pH of 3 and shaken at 200 rpm and room temperature. The applicability of the pseudo-first order equation to experimental data generally, differs in two ways; the parameter does not represent the number of available sites and the parameter $\log(q_e)$ is an adjustable parameter and often found not equal to the intercept of the plot $\log(q_e - q_t)$ versus t, where as in true first order, $\log(q_e)$ should be equal to the intercept.as it can be observed from the graphs. The lower correlation coefficients obtained suggest that the adsorption of fluoride ion on the adsorbent hydroxyapatite does not follow the pseudo first order kinetics.

4.8.2. Pseudo-second order kinetic model

The pseudo-second-order adsorption kinetic rate equation is expressed in linearized integral form as;

$$\frac{t}{q_t} = \frac{1}{k_2 qe^2} + \frac{1}{qe}(t) \quad \text{..... equ. (4.2)}$$

The values of (t/q_t) were linearly correlated with t and gave a linear relationship from which $q_e$and K_2 can be determined from the slope and intercept of the plot, respectively.

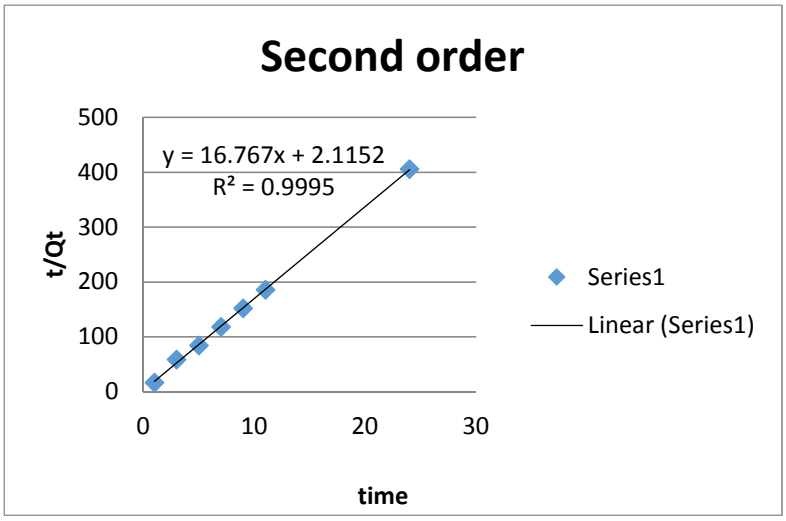

Figure 14 Pseudo Second Order Kinetic result.

Table 6.adsorption kinetics parameter for pseudo second order

Pseudo Second order Kinetics	Intercept	K_2	R^2	Q_e
	2.1152	134.048	0.999	0.0596

From the result of adsorption kinetic first order and second order data, it is possible to summarize the adsorption behavior of the adsorbents prepared. The correlation coefficient (R^2) was found to be 0.0089 and 0.999 for pseudo first-order kinetics and pseudo second-order kinetics respective. The value of R^2 for pseudo second-order kinetics approaches to one. This indicated that it is unity and the adequate linear fitting of the plots confirmed that the adsorption of fluoride ions using the

synthesized hydroxyapatite followed pseudo second order kinetics. Calculated equilibrium adsorption capacity qe (cal), pseudo second-order rate constant and the initial adsorption rate were obtained from the model. The experimental equilibrium adsorption capacity and the calculated capacity are close to R^2value of 0.999. This rate expression was used to describe chemisorption involving valiancy forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces, and ion exchange [80]. Similar results have been reported by other researches [81].

4.8.3. pH at the potential of zero zharge (pHpzc) determinations

pH_{pzc}, is the pH value at the point where the net surface charge of the adsorbent is 0. pH_{pzc} values for the synthesized HA powder at optimized operational parameter is around 7.90. The pH values of the adsorbents generally fall in the acidic and slightly neutral region and values of $pH_{pzc}<8$ show dominancy of acidic groups over basic groups. The net surface charge of the adsorbents under pHpzc is positive, while it is negative above pHpzc. Therefore, knowledge of this value helps to decide at which pH value one should work during adsorption studies. Hence the adsorbent percent removal capacity increases below pH_{pzc} value [82].

Table 7 ΔpH vs. pH final of the adsorbent perfumed on 2g HA, 10mg/L of fluoride concentration and 5hr. Contact time

Initial pH	2	3	4	5	6	7	8	9	10	11
Final pH	2.90	3.60	4.50	5.40	6.30	7.21	7.90	8.30	8.90	9.86
Change in pH	0.90	0.60	0.50	0.40	0.30	0.21	0	-0.7	-1.1	-1.14

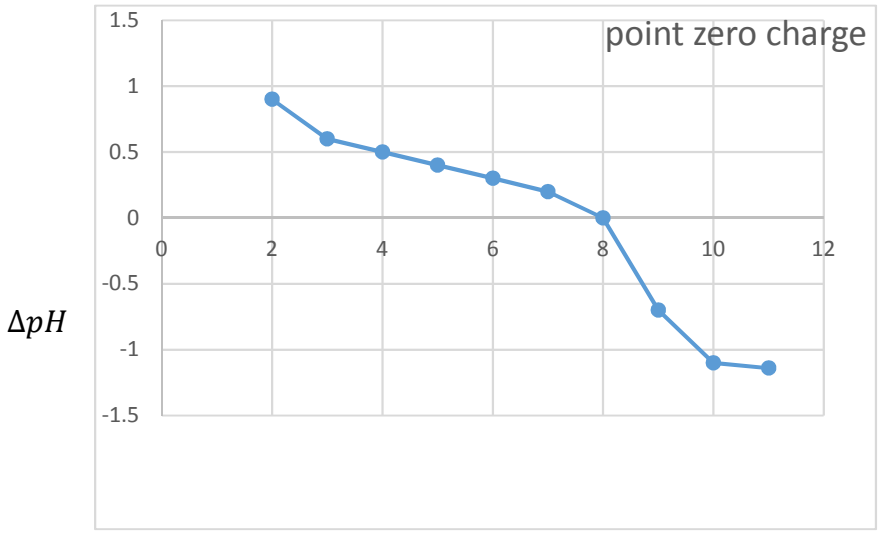

Figure 15: Plot of ΔpH vs. pH final of the adsorbent to determine zero point charge.

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In this work, phase pure hydroxyapatite was synthesized from eggshell at two steps calcination through precipitation reaction for defluoridation of water by adsorption. One of the main advantages of the method is that water is the only by-product. XRD result revealed the synthesized HA powder was phase pure with hexagonal structure. The prepared adsorbent was applied to the real water samples under optimized conditions and found to be effective with good fluoride removal efficiency (or greater than 80%).

5.2. Recommendation

Naturally, raw water contains an ions that compact with fluoride for adsorption such as HCO_3^- $SO4^{2-}$ and Cl^- etc. The effect of these co-ions should be investigated so that it helps to selectively use the adsorbent in preference to other ions.

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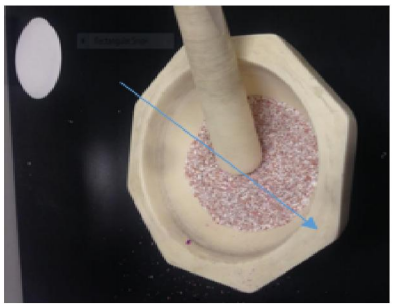
APPENDIX

3.2.2 Laboratory Performance process block diagram supported by Photo.

Parte 1 Synthesis of Calcium precursor CaO from Eggshells. (step 1-4)

Egg shell was washed

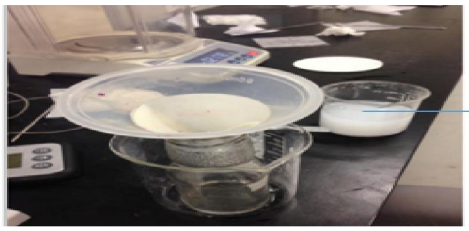
Boling in distilled water



Garinding in mortar and pistil

calcined in furnace

Parte 2 Synthesis of Calcium precursor CaO from Eggshells. (step 5-10)



OROMO SELF-HELP ORGANIZATION (OSHO)
WALDA OF GARGAARSA OROMOO

Our Ref. No. OSHO/RVDHP/550/18

Date 02/03/18

To: Adama science and Technology University (ASTU)

Adama

Subject:- sending fluoride chemical analysis test result.

As it might be recalled, you have requested our center to support **Mr.Kifle workeneh** for fluoride concentration test with letter dated on **14/06/2018** and Ref No **ChemD/383/2018**.
Accordingly ,**Mr.Kifle workenew** has been working on the analysis samples he brought for with our lab technician in our technology center.
Please find enclosed here with three **(3) pages** lab results produced by our lab technician for the samples brought to our center.

With regards,

Getachew Hallo
Chief Executive Office

Address: Tel. 53 69 62, 53 73 03 - 06 Fax 00251-1-536967 P.O.Box 1214 Addis Ababa E-mail OSHO@ethionet.et

Fluoride Removal Technology Center

TO: Chief executive officer of OSHO

FROM: laboratory section

Target: To reveal the laboratory results for defluoridation test of HAp (hydroxyapatite powder) Synthesized from Eggshell for the student KifleWorkeneh who studying in ASTU, post graduate (MSC) and Performed his project in our lab.

Optimization is Maximizing or Minimizing of one parameters to obtained the desired value .in this case higher efficiency while keeping the other parameters constant

1, Application of HAP on Laboratory prepared known fluoride Solution.

A / To know effect of dosage,

Varying dose ,at constant (contact time ,PH initial fluoride concentration of solution and Volume of water.)

Time (hr)	PH	Dosage (g) HAP	Initial Conc.of F (mg/l)	Residual conc.of F mg/l	Percentage removal	Adsorption capacity	Rremark
5	3	1	10	0.49	95.1		
5	3	3	10	0.11	98.9		
5	3	5	10	0.10	99		
5	3	7	10	0.09	91.1		

B/ To know the effect of contact time,

Varying the contact time at constant (HAP dose, PH, Concentration of fluoride in the solution,Volume of water)

Time(hr)	PH	Dosage (g) HAP	Initial Conc. of F- ¯mg/l	Residual conc F – Mg/l	Percentage removal	Adsorption capacity	Remark
1	3	5	10	0.15	98.5		
3	3	5	10	0.12	98.8		
5	3	5	10	0.10	99		
7	3	5	10	0..11	98.9		
9	3	5	10	0.11	98.9		
11	3	5	10	0.13	98.7		
24	3	5	10	0.13	98.7		

HailuNegu

Fluoride Removal Technology Center

C / To know the effect of fluoride concentration

Varying the initial concentration of fluoride in water prepared in laboratory at constant PH, HAP dose, volume of water, contact time), and observing residual concentration.

Time (hr)	PH	Dosage(g) HAP	Concentration of F-in 30ml sample water-mg/l	Residual conc, F-mg/l	% of F-removal	Adsorption capacity	Remark
5	3	5	5	0.25	98.75		
5	3	5	10	0.50	95		
5	3	5	15	0.96	93.6		
5	3	5	20	1.6	92		

D / to Know effect of PH,

Varying the PH, at a constant (fluoride concentration, contact time , HA dose &volume of water)

Time (Hr)	PH	Dosage (g)	Initial Conc.of F (mg/l)	Residual conc.of F mg/l	% removal	Adsorption capacity	Remark
5	3	5	10	0.12	98.8		
5	5	5	10	0.26	97.4		
5	7	5	10	1.5	85		
5	9	5	10	1.2	88		

2, Application on Raw water test

A / to know effect of HA dose on Bofo water.

Varying dosage, at constant (time, PH and concentration of solution,volume of water)

Time (hr)	PH	Dosage (g) HAP	Initial Conc.of F (mg/l)	Residual conc.of F mg/l	Percentage removal	Adsorption capacity	Remark
5	7	1	8.3	2	75.90		
5	7	3	8.3	1.8	78.31		
5	7	5	8.3	1.5	81.92		

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