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DEVELOPMENT OF A POINT OF USE WATER PURIFIER USING ALUMINIUM OXIDE-BASED FLOCCULENT-DISINFECTANT COMPOSITE

MASTER OF SCIENCE IN WATER MANAGEMENT

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Development of a Point of Use Drinking Water Purifier using Aluminium Oxide-Based Flocculent-Disinfectant Composite

By

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A thesis submitted to the African Centre of Excellence for Water Management (ACEWM) in partial fulfilment of the requirement for Master's Degree in Water Management (Water Quality Management) of Addis Ababa University

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CERTIFICATE OF APPROVAL

The undersigned, certify that this thesis titled ***Development of a Point of Use Drinking Water Purifier Using Aluminium Oxide-Based Flocculent-Disinfectant Composite*** is a result of the authors work, and that to the best of our knowledge it has not been submitted for any other academic qualification within Addis Ababa University or elsewhere. The thesis is acceptable in form and content, and that satisfactory knowledge of the field covered by thesis was demonstrated by the candidate through oral examination held on 18th June 2021 at African Center of Excellence for Water Management (ACEWM) Addis Ababa University, Ethiopia.

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I, **Patricia Namate**, declare that this thesis report is my original effort and work and to the best of my knowledge, the findings have never been previously presented to Addis Ababa University or elsewhere for the award of any academic qualifications. Where assistance was sought, it has been accordingly acknowledged. The findings, interpretations and conclusions expressed in this study neither reflect neither the views of the Addis Ababa University nor those of the African Centre of Excellence for Water Management (ACEWM) nor those of the individual members of the MSc Examination Committee.

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DEDICATION

I dedicate this study to my late brother Weston Namate, who passed away on 10Th February 2021. For the sweet memories we shared.

ABSTRACT

The United Nations officially declared access to clean drinking water and sanitation to be a human right in 2010. Despite this, one in every three people in the world still lacks access to clean drinking water. A lot of people suffer from water-borne diseases as a result of contaminated drinking water. Aside from microbiological pollution, high fluoride content in drinking water is one of the most serious problems in African countries. The present study aimed to contribute to the availability of clean water by developing a point of use drinking water purifier using aluminium oxide-based flocculent-disinfectant composite. The study involved the preparation of aluminium oxide (AO) prepared from locally available aluminium sulphate (alum) using a standard method. This was followed by batch experiments to investigate different parameters that affect the efficiency of fluoride removal and E. coli log reduction by the developed method. A dose of 75mg/L AO, 800 mg/L alum, 35% lime and 1.5 mg/L calcium hypochlorite achieved 95% fluoride removal efficiency and 5 log 10 reduction of *E. coli* using 15 mg/L as initial fluoride concentration and 10^5 CFU/100 mL *E. coli* concentration. The optimum contact time was found to be 30 minutes. Initial fluoride concentration affected fluoride removal but showed no effect on E. coli inactivation. The optimum pH of the solution for both fluoride removal and *E. coli* log reduction was found to be in the range of 4-8. *E. coli* concentration did not affect fluoride removal. The fluoride removal efficiency and *E. coli* log reduction were tested on real water samples from the Ethiopian Rift Valley. The results showed that water samples from Rift Valley required a high dose of alum, AO and calcium hypochlorite and a low dose of lime. Three prototypes were developed as high dose, medium dose and low dose for treating water samples with 5 mg/L, 10 mg/L and 15 mg/L fluoride concentrations. The prototypes are powdered form packed in sachets. The high, medium and low doses weigh 11.9 g, 10.6 g and 9.9 g, respectively. The prototypes were tested on real water samples from the Ethiopian Rift Valley and the results were found to be within the drinking water standards. The present study showed that the developed product has the potential to purify drinking water contaminated with fluoride and disease-causing microorganisms. This study suggests that the product should be tested at a pilot scale and upon its success, the product could be manufactured at a larger scale to which communities without access to portable water would use the product for treating drinking water at a household scale.

Key words: Fluoride removal, *E. coli* inactivation, Ethiopian Rift Valley, Point of use water treatment, and Batch experiments.

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ABBREVIATIONS AND ACRONYMS

AO	Aluminium Oxide
BSF	Bio Sand Filter
CDC	Centers for Disease Control and Prevention
CFU	Colony Forming Unit
CDPs	Coagulant/Disinfection Products
EPA	Environmental Protection Agency
E. coli	Escherichia Coli
FCR	Free Chlorine Residual
HWT	Household Water Treatment
NBS	National Bureau of Standards
NF	Nano Filtration
PVP	Polyvinylpyrrolidone
POU	Point of Use
PET	Polyethylene Terephthalate
PSI	Population Services International
PZC	Point Zero Charge
RO	Reverse Osmosis
TDS	Total Dissolved Solids
SDGs	Sustainable Development Goals
SODIS	Solar Disinfection
UNDP	United Nations Development Program

UNESCO	United Nations Educational, Scientific and Cultural Organization
UNICEF	United Nations Children’s Fund
UNPF	United Nations Population Fund
UV	Ultraviolet
WHO	World Health Organization
WWAP	World Water Assessment Program

1. INTRODUCTION

1.1. Background of the study

Lack of access to safe drinking water is one of the world's largest health and environmental problems (Sobsey, et al, 2008). Even people with "improved" water sources, such as household connections, public standpipes, and boreholes, may not have water that is microbiologically and chemically safe (Duke, Nordin, Baker, & Mazumder, 2016). The water sources contain microorganisms that cause a variety of illnesses such as cholera, diarrhoea, dysentery, hepatitis A, typhoid, and polio. The water sources also contain ions such as fluoride, arsenic that cause health problems such as fluorosis. Unsafe water also worsens malnutrition, particularly childhood stunting (Sharma & Bhattacharya, 2017).

Africa seems to have plenty of water with a lot of ponds, huge wetlands, widespread groundwater and lakes (Bhatnagar & Minocha , 2006). Similarly, rainfall is abundant, with average annual rainfall in Africa equal to those in Europe and North America (Bogale, 2020). The usability of these water supplies relies on the quality of the water. Water quality is influenced by natural processes, such as seasonal trends, underlying geology and hydrology, weather and atmosphere, and human factors, including domestic, agricultural as well as manufacturing of different products (UNDP, 2006). Water infected by microbiological toxins spreads diseases. Apart from microbial contamination, a high concentration of fluoride in drinking water is also one of the biggest challenges in African countries. Groundwater in some parts of the African countries contains fluoride in concentrations exceeding the 1.5 mg/L permissible limits established by the WHO (Kut, Sarswata, Srivastava, & Pittman , 2016)

Point-of-use (POU) water treatment technology has evolved as a method for empowering people and communities without access to clean drinking water to improve water quality by treating it at home (Mwabi & Adeyemo, 2011). Studies on water, sanitation, and hygiene initiatives have shown that POU interventions are more successful than source interventions in improving water quality (CDC, 2012). Studies suggest that improving home drinking water quality at the POU can reduce diarrheal illness by 30-40% (Holtslag & Mekonta, 2014). There are a variety of POU technologies from which policymakers, implementers, and users can choose as appropriate for certain conditions and demographics. The choice of acceptable technologies is dependent on the characteristics of raw water (i.e., the quality and degree of contamination), facilities (i.e. electricity, manpower, supply of chemicals), affordability/cost and acceptability (Sharma & Bhattacharya, 2017).

Although many POU technologies have been proposed, tested, and distributed, not all have solid evidence-based effectiveness and long-term usage (Sobsey, *et al*., 2008). One of the barriers to making informed decisions regarding the broad adoption of these technologies is a lack of robust scientific proof of long-term use, good health effects, and water quality improvement. Water guard, PUR, aqua tabs, and Bishan Gari are examples of POU products that have been documented to have demonstrated microbiological and chemical effectiveness (Holtslag & Mekonta, 2014).

Globally, water guard is a POU water purifier that was developed by Population Services International (PSI) (NBS, 2010). Water Guard is dilute sodium hypochlorite (chlorine) solution used to disinfect drinking water in the home. One capful of solution treats approximately 20 litres of water, which is the size of the majority of containers used to acquire and store water in most rural households. It effectively kills viruses and bacteria in drinking water. The treatment is simple to apply and affordable – a bottle often costs less than thirty cents to protect a family of six for one month. It is effective in killing bacteria and viruses. However, according to Holtslag & Mekonta, (2014), the shortfalls of water guard include short shelf life (3-6 months), inability to eliminate cryptosporidium, a leading cause of death in children under the age of five, it does not remove dirt or particulates and most individuals dislike the smell/taste.

In a pursuit to improve microbial quality of water and reduce turbidity, in collaboration with the Centers for Disease Control and Prevention, the Procter & Gamble Company (P&G) created the PUR Purifier of WaterTM. PUR sachets are currently mass-produced in Pakistan and marketed to non-governmental organizations across the world (CDC, 2012). PUR is a small sachet of powdered ferric sulphate (a flocculant) and calcium hypochlorite (a disinfectant). PUR was created to reverse-engineer a water treatment plant, combining several particle removals and disinfection barrier techniques. CDC (2012) stated that PUR has the following benefits: bacteria, viruses, and protozoa have all been shown to be reduced in water, water is protected from contamination on a long-term basis, proven health benefit, users accept the water because of the aesthetic enhancement, and sachets are readily transported because of their compact size, and extended shelf life. On the other hand, Holtslag & Mekonta, (2014) stated that PUR needs to be imported and does not reduce fluoride levels to below 1.5 mg/L for water sources that have high fluoride concentrations.

Locally, Bishan Gari was developed in Ethiopia by Bishan Gari purification industries (Bogale, 2020). It removes turbidity, organic debris, and microorganisms by flocculation and settling, thereby enhancing the appearance of the water and increasing the efficiency of chlorine. Bishan Gari has the following advantages according to Holtslag & Mekonta, (2014): a longer shelf life than liquid chlorine, a small volume that makes it simpler to carry and store, it is locally made, and it is inexpensive. The downsides of Bishan Gari are as follows: does not reduce fluoride levels to below 1.5 mg/L for water sources with fluoride concentrations of above 10 mg/L and people do not like the smell of the treated water (Holtslag & Mekonta, 2014).

Various technologies have been developed worldwide including in Ethiopia to reduce fluoride concentration in drinking water. The coagulation and adsorption/ion-exchange methods are still the most extensively employed fluoride removal procedures in developing-world endemic regions (Ayoob, Gupta, & Bhat, 2008). Coagulation is a process that includes the precipitation or co-precipitation of fluoride utilizing appropriate reagents such as lime, calcium and magnesium salts, poly aluminium chloride, and alum (Yang & Dluhy, 2002). Coagulation has the advantage of being a simple and inexpensive procedure. Demerits of coagulation include medium efficiency (70%), large dose requirement, and residual sulphate salinity, hardness of treated water, increased pH, and excess residual aluminium. Adsorption is another key way of removing excess fluoride from aqueous solutions. By properly exploiting the capacity of an adsorbent bed, a packed bed of adsorbent in stationary columns is continually employed for cyclic sorption and/or desorption of pollutants in this process (Dubey, Agrawal, & Gupta, 2018). The pollutant is concentrated and limited to a tiny adsorbent mass from a relatively substantial liquid volume, which may invariably be regenerated, reused, or securely disposed of under control (Rao & Viraraghavan, 2002). Bone char, activated alumina, activated carbon, activated bauxite, ion-exchange resins, fly ash, super phosphate and tricalcium phosphate, clays and soils, synthetic zeolites, and other minerals are common adsorbents(Ayoob, *et al*., 2008). The problems of regeneration, the poor capacity of less purified technical-grade products, the comparatively high price of some adsorbents, and other adsorbents, such as bone char, are restrained by community religious beliefs (Dubey, *et al*., 2018).

The most common POU technologies that have been developed so far do not simultaneously kill microbes and reduce fluoride levels for water sources with fluoride concentrations of above 10 mg/L.

1.2. Problem statement

The vast majority of people, particularly in rural regions, lack access to safe drinking water (Tangui, *et al*., 2019). Because of the high cost of treated water, they are forced to rely on easily available supplies, which are therefore of poor quality, exposing them to waterborne diseases and many health underlying issues (Bogale, 2020). The SDGs' six "outcome-oriented goals" include safe and affordable drinking water as well as improved water quality (WHO/UNICEF, 2017). However, Ethiopia and other developing countries continue to lag far behind in providing improved water, especially to rural communities (Andualem, *et al*., 2021).

Due to a scarcity of piped water, initiatives into alternate Point of Use (POU) technologies have occurred (Sobsey *et al*., 2008). Various POU methods such as filtration, solar disinfection (SODIS), coagulation, chlorination, and flocculation have been extensively studied and reported. Coagulant/disinfection products (CDPs) have the distinct benefit of offering microbial quality recovery, turbidity reductions, and a post-treatment free chlorine residual (FCR) among the various available point of use (POU) techniques (e.g., boiling, household chlorination, ceramic filtration) (Clasen, *et al.*, 2006). These are available in readily available sachets that contain at least two main active ingredients (typically in powdered form), namely a coagulant (e.g., aluminium or ferric salt) and a disinfectant (i.e. chorine variant). Examples include PUR, Bishan Gari as well as Aquatabs (Bogale, 2020). The combination of aluminium sulphate and calcium hypochlorite in these water purifiers also reduces fluoride levels in drinking water. The insoluble aluminium hydroxide flocs formed during this process is responsible for the co-precipitation of the fluoride ions, a technique called Nalgonda (Dubey *et al*., 2018). However, this method is not suitable for treating water with high total dissolved solids (TDS) and raw water fluoride concentration exceeding 10 mg/L (Ayoob, *et al*., 2008). This means that the communities using water with fluoride concentrations exceeding 10 mg/L will still be exposed to high fluoride concentrations even after using the available water purifiers because these water purifiers reduce fluoride levels using the Nalgonda technique.

In addition, the aforementioned water purifiers generate a lot more sludge after treatment since the technologies consume more aluminium sulphate dose to reduce the fluoride to its permissible level and some of the water purifiers do not effectively treat turbid water (CDC, 2012). Hence, there is a need to look for a solution to minimize the amount of sludge produced after treatment and also effectively treat turbid water.

Research conducted by Mulugeta *et al*., (2014) compared the performance of the commercially available aluminium oxide and aluminium oxide synthesized in the laboratory and showed that the fluoride removal capacity of AO synthesized in the lab was twice that of the commercially available aluminium oxide materials such as activated alumina and boehmite.

The challenges associated with existing POU water purifiers suggests further research on the development of a water purifier that addresses the problems of sludge generation after treatment, ineffective treatment of turbid water and ineffective fluoride removal of fluoride for water sources with above 10 mg/L fluoride concentrations. Therefore, the present study seeks to address these challenges associated with the existing POU purifiers` by combining aluminium oxide synthesized in the laboratory using the recommended method with a proper disinfectant

1.3.Research objectives

1.3.1. Main Objective

The main objective of this study was to develop a point of use drinking water purifier using aluminium oxide-based flocculent-disinfectant composite.

1.3.2. Specific Objectives

The specific objectives of this study were as follows:

- To synthesise aluminium oxide (AO) using the standard method and conduct batch fluoride and bacterial removal experiments using the synthesized AO, aluminium sulphate, calcium hypochlorite and lime under optimized conditions,
- To test the composite on real water samples from the Ethiopian Rift Valley region,

- To develop a prototype household water purifier using aluminium oxide-based flocculent-disinfectant composite, and
- To perform Physico-chemical analysis of treated water using the developed product

1.4. Research questions

In pursuing the above objectives, the study tried to answer the following questions:

- What are the different process parameters that affect fluoride removal and E. coli inactivation?
- How is the technology performing on real water samples from the Ethiopian Rift Valley?
- In what ways can a water purification prototype product be developed?
- How is the quality of the treated water using the developed product?

1.5.Significance of the study

This study helps improve both the microbiological and chemical quality of water by utilizing a simple product to treat water polluted with bacteria and with fluoride concentrations exceeding 10 mg/L at the point of use. The study developed a point use water purification product using aluminium oxide synthesized in the lab using the standard method and calcium hypochlorite as a disinfectant. Studies have shown that this aluminium oxide has a high fluoride removal capacity and can effectively treat water with fluoride concentrations of above 10 mg/L. This type of research is among the few studies striving to improve both microbial and chemical quality of water since most water treatment products utilized in Ethiopian rural communities do not contain aluminium oxide and do not effectively treat water with fluoride concentrations above 10 mg/L and high total dissolved solids, thus it adds to the body of scientific knowledge at the national level.

In practice, the study has the potential to develop a product that can be used in rural settings where people use contaminated water for domestic purposes or where there is recontamination due to storage and unhygienic practices since the treated water analysed for different parameters were within the permissible drinking water standards. This would allow policymakers and other stakeholders to evaluate the developed product at a pilot scale, and if successful, the product could be manufactured at a bigger scale and suitable methods for wide-scale usage of the treatment choices implemented. Sensitization sessions with communities will be held to emphasize the need for purifying water at home. Through policy, communities can be urged to utilize the product to decrease challenges associated with drinking water from polluted sources.

1.6.Scope and limitation of the study

The study aimed at developing a point of use household water purification product that can be used to disinfect water, reduce turbidity and reduce fluoride levels in drinking water. The study involved experiments on the synthesis of aluminium oxide and batch experiments of different parameters that affect fluoride removal and microbial inactivation (dose, contact time, pH, and initial E. coli concentration and fluoride concentration). The technology was tested on real water samples from the Ethiopian Rift Valley to find a combination of chemicals that can achieve both microbial inactivation and fluoride removal. The study developed a prototype water purification product in a powder form that was packed in a sachet. Finally, the study tested the performance of the developed product to assess its suitability for drinking purposes by analysing the treated water for the following physicochemical parameters: turbidity, E. coli, pH, fluoride, alkalinity, sulphate, aluminium, chloride, residual chlorine and electrical conductivity. The drinking water parameters were compared with WHO drinking water standards.

The study did not assess the concentrations of the disinfection by-products formed in the water treatment process due to a lack of equipment for quantifying the by-products.

2. LITERATURE REVIEW

2.1.The concept of Household Water Treatment (HWT)

Household Water Treatment (HWT) and safe storage technologies are some of the devices or methods used for the treatment of water in the home or at the point of use in other settings (Mwabi & Adeyemo, 2011). These are also referred to as point-of-use (POU) water treatment technologies (Ngasala, *et al*., 2020). HWT technologies include a range of options that allow individuals and communities to treat collected water for the removal or inactivation of microbial pathogens (Pearson, *et al*., 2016). There are also many devices and products on the market that remove different contaminants from drinking water. Household water treatment (HWT) plays a significant role in protecting public health from numerous water-related diseases in places where people use water from unimproved supplies of water for domestic purposes, where water is polluted during delivery, or where water is not properly handled (Mwabi & Adeyemo, 2011). Research has shown that easy and affordable methods of household water treatment can improve the quality of drinking water and reduce a variety of diseases caused by drinking water contamination (Sobsey *et al*., 2008).

Mwabi & Adeyemo, (2011), explains that household water treatment can be used in cases where the drinking water is contaminated and there is no solution present. The choice of the suitable technology will depend on the situation, the condition of the raw water, the availability of the materials and equipment, the period during which it is to be used, the local population's customs, expectations and educational levels, and the availability of staff to provide the required training and supervision to ensure that the technology is effectively applied.

2.2. Methods for Household Water Treatment

The objective of household water treatment is to treat contaminated drinking water so that the microbial and chemical water content should be within the permissible standards (Mohapatra et al., 2009). For water purification, many methods have been published. Below, some of the approaches are discussed.

2.2.1. Disinfection

Unlike many other treatments that remove germs from water, disinfection involves the inactivation or killing of disease-causing microorganisms in water (Ratnayaka, Brandt, & Johnson, 2009). Because numerous types of microbes are present in water sources, the kind of disinfectant and dosage/exposure duration vary depending on the microorganism. Furthermore, various disinfectants have various processes for microbial inactivation/destruction. The method used to disinfect water for human consumption is determined by a variety of variables. These include its efficacy against waterborne pathogens (bacteria, viruses, protozoa, and helminths); the precision with which the process can be monitored and controlled; the ability to produce residues that provide an added measure of protection against possible post-treatment contamination caused by the distribution system faults, the esthetic quality of the treated water, and the cost of treatment (Pooi & Ng, 2018). Solar disinfection and chemical disinfection are two of the most often used disinfection methods (Mwabi & Adeyemo, 2011).

2.2.1.1. Solar Disinfection (SODIS)

Solar disinfection (SODIS) is a low-cost efficient disinfection POU that includes exposing water in polyethene terephthalate (PET) or glass to sunshine for an extended period. (Venkatesha, Rao, & Kadare, 2020). The SODIS mechanism is based on a combination of solar radiation effects, namely thermal heating and ultraviolet (UV) light (McGuigan, *et al.,* 2012). The pathogens in the water are therefore inactivated as a consequence of synergistic actions. However, UV-A radiation (320 – 400 nm) is thought to be the predominant contributor since the wavelengths of UV-A induce DNA damage in pathogens, killing the germs (Haider, *et al*., 2014). Figure 1 depicts a representation of the SODIS process and its underlying mechanism.

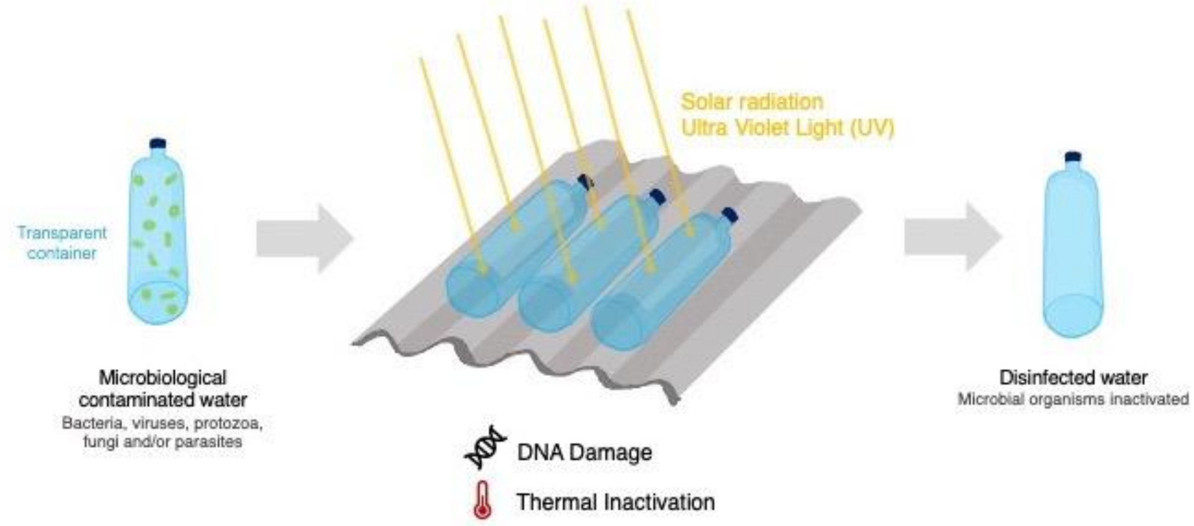

Figure 1: SODIS process and its underlying mechanism

Source: Haider, *et al*., (2014)

Studies have been done on SODIS. Wegelin, *et al*., (2014) discovered that once water temperature rises beyond 40°C, Vibrio cholera becomes inactive. *E. coli* was discovered to be somewhat more heat resistant. When the water temperature was over 45°C, *E. coli* concentration decreased. However, temperature alone is insufficient to disinfect the water supply. In another research, a transparent container performed somewhat better than a completely black bottle (negating UV effect), although the temperature within the transparent container was lower. Coliforms were not discovered in the clear container after 4 hours of sunlight exposure, but they were discovered in the black bottle (Martín, *et al*., 2005). SODIS also works well in murky water as well. Although turbidity lowered the efficacy of UV transmittance, UV light scattering inside the bottle boosted efficiency. Another study found that SODIS could disinfect and achieve a 6-log reduction for E. *coli* from well water with turbidity up to 100 NTU (Wegelin, *et al*., 2014). While the treatment process is straightforward, consumers will be dissatisfied with the length of time required to treat water. Unless pretreated, SODIS disinfection is ineffective with highly turbid water (Wanjiru, 2015).

2.2.1.2. Chemical disinfection

Chemical disinfection involves the use of chemicals to kill or inactivate pathogens in water supply systems. The most common chemicals used in disinfection include chlorine, chloramine (monochloramine) as well as (Owoseni, Olanirani, & Okoh, 2017). Chlorination is considered a simple, affordable and scalable method of water disinfection through the use of sodium hypochlorite NaOCl (liquid) and calcium hypochlorite $Ca(OCl)_2$ (solid). It is effective against many pathogenic bacteria, but it does not destroy all viruses, cysts, or worms at standard doses. According to Imodagbe, (2013), the three primary pathogen inactivation mechanisms are as follows: by attacking important cell elements, such as the cell wall or the functioning of semi-permeable membranes there by damaging or degrading cellular structural order, interfering with energy-producing metabolism by combining enzyme substrates with prosthetic groups of enzymes, leaving the enzymes inactive and; by inhibiting the creation of normal proteins, nucleic acids, coenzymes, or the cell wall there by interfering with biosynthesis and development. Table 1 lists the chemical disinfection techniques, as well as their primary benefits and drawbacks.

Table 1: Basic disinfection processes, their advantages and limitations

Disinfection Process	**Advantages**	**Limitations**
Chlorination	Effective disinfectant; residual in the distribution	Formation of by-products; loss of residue as water storage time increases
Chloramination	The residue is stable, and there are fewer odour and taste concerns.	Less efficient disinfection; requires strict process control to minimize taste and odour problems.
Chlorine dioxide	At higher pH levels, it is more effective than chlorine and has fewer by-products.	Formation of inorganic by-products
Ozone	Effective disinfectant	Inefficiency; difficult to process; costly technology

Source: Tsitsifli & Kanakoudis, (2018)

2.2.2. Coagulation and flocculation

Coagulation and flocculation are low-energy, long-lasting water treatment methods. Coagulation is defined as the destabilization of tiny particles (0.01–1 m) that results in the creation of bigger particles. The development of flocs from destabilized particles is referred to as flocculation (Metcalf & Eddy, 2003). After that, the flocculated particles can be removed by settling or filtering.

Turbidity, colloids, and protozoan cysts are successfully removed by coagulation (Preston, Lantagne, Kotlarz, & Jellison, 2010). Coagulation, on the other hand, is incapable of achieving stable coliform removal. To increase total pathogen elimination efficiency, it must be combined with additional treatment processes (Crump, 2014). When employed as a pretreatment or in conjunction with a membrane process, coagulation can increase the removal of Cryptosporidium, E. coli, and many other diseases. Furthermore, coagulation will improve the disinfection process by eliminating turbidity and reducing disinfectant scavenging by natural organic matter (Metcalf & Eddy, 2003)

Several chemicals have been used as coagulants. These include aluminium sulphate, iron salts as well as lime (Pooi & Ng, 2018). The use of these coagulants necessitates extensive training and technical expertise. As a result, it was largely used for community purposes in rural areas in the past. Coagulant use in the home is uncommon (Souter, 2003). However, the optimization of coagulant dosage, the development of natural coagulants, and the addition of disinfectants have enabled manufacturers such as Procter & Gamble Co. (P&G) and Poly Glu International Co. to produce coagulants/flocculants called PUR that are stored in small POU sachets (CDC, 2012). This facilitates usage and distribution. The PUR sachet is a flocculation/disinfection system in one (Pooi & Ng, 2018). In research conducted in western Kenya, P&G sachets of varying doses were used to treat turbid water from diverse sources. The study found that a high dosage formulation of the flocculant-disinfectant product produced water with a mean *E. coli* concentration of 0 CFU/mL. When employed in high turbid water, the low dosage formula was unable to consistently reach drinking water quality. In rural Guatemala, the usage of P&G's flocculant-disinfectant sachet reduced diarrhoea episodes per person by 23.8%. (Reler, 2003).

Coagulation is also used to remove fluoride from drinking water (Dubey, *et al.*, 2018). The Nalgonda technique, created by the National Institute of Environmental Engineering Research (NEERI), is one of the most widely utilized defluoridation procedures in India, particularly at the community level (Ayoob, *et al.*, 2008). It has been used in underdeveloped countries to defluoridate water (e.g., India, Ethiopia, Kenya, Tanzania and Senegal). The Nalgonda procedure is a coagulation-precipitation-sedimentation-filtration mechanism based on aluminium sulfate (Dargahi, Atafar, Mohammadi, Azizi, Almasi, & Ahagh, 2016). To ensure full mixing, alum ($Al_2(SO_4)_3.18H_2O$) is applied as a coagulant to the fluoride-contaminated water under efficient mixing conditions in the Nalgonda technique. This causes the formation of insoluble aluminium hydroxide ($Al(OH)_3$ micro-flocs, which aggregate to form large settleable flocs. Fluoride is removed by electrostatic attraction of negatively charged fluoride ions (F^-) in solution onto aluminium hydroxide particles, which are then isolated from the water by sedimentation and filtration (Dysart, 2008). When alum is mixed with water, the solution becomes acidic. To achieve a neutral pH, simultaneous addition of lime ($Ca(OH)_2$) is needed (Fawell & Nieuwenhuijsen , 2003).

According to Fawell & Nieuwenhuijsen, (2003), the various reactions which occur in the Nalgonda defluoridation process are presented by the following equations

Dissolution of Alum:

$$\boldsymbol{Al_2(SO_4)_3 18H_2O \rightarrow 3Al^{3+} 3SO_4^{2+} + 18H_2O} \qquad (1)$$

Precipitation of aluminium hydroxide:

$$\boldsymbol{2Al^{3+} + 6H_2O \rightarrow 2Al(OH)_3 + 6H^+} \qquad (2)$$

Co-precipitation of fluoride:

$$\boldsymbol{F^- + Al(OH)_3 \rightarrow Al - F\ complex + undefined\ product}) \qquad (3)$$

pH adjustment:

$$\boldsymbol{6Ca(OH)_2 + 12H^+ \rightarrow 6Ca^{2+} + 12H_2O} \qquad (4)$$

Some limitations/shortcomings of the Nalgonda defluoridation technique include:

- The technique's performance is limited to roughly 70%. As a result, it is not appropriate in situations where the fluoride concentration of raw water is excessively high (Fawell & Nieuwenhuijsen, 2003);
- The Nalgonda approach has high maintenance costs (Meenakshi & Maheshwari, 2006);
- To ensure successful fluoride removal, the procedure necessitates proper chemical dosing, routine presence, and close supervision. UNICEF has identified rural communities as having labour, expertise, and time needs that are difficult to meet on a sustainable basis (Fawell & Nieuwenhuijsen, 2003);
- It generates toxic sludge that must be disposed of properly;
- When aluminium sulphate is used as a coagulant, the sulphate ion concentration rises, which might elicit cathartic symptoms (accelerated defecation) (Meenakshi, Sundaram, & Sukumar, 2008);
- The method may need a considerable amount of aluminium sulphate, and consumers may complain about the flavour of the treated water (Fawell & Nieuwenhuijsen, 2006). As a result, customers have the option of bypassing the treatment unit and using raw water directly, or they can revert to their traditional and polluted water sources.
- Excess residual aluminium in treated water due to the technique's usage of aluminium sulphate can produce detrimental dementia illness as well as neurobehavioral, structural, and biochemical abnormalities. It can also affect the respiratory, digestive, endocrine, and reproductive systems. Excess aluminium in beverages has also been linked to Alzheimer's disease causes (Sajidu, Kayira, Masamba, & Mwatseteza, 2012).

2.2.3. Filtration

Filtration is a straightforward water treatment method that removes colloids, suspended particles, and microorganisms from drinking water sources. Size exclusion is its primary elimination strategy. A well-designed filtration system can provide a clean stream of drinking water. Bio sand filtration (BSF), bone-char filters, and membrane filtration are the most common filtration methods used in POUs (Bhatnagar & Minocha, 2006).

2.2.3.1.Bio sand filtration

BSF is a promising POU treatment method that has been used by over 500,000 individuals globally (Bhatnagar & Minocha, 2006). It is simple to build and may be done using locally produced basic materials. The BSF principle is similar to that of a traditional slow sand filter. BSF, on the other hand, has varied flow rates and intermittent filtering through the sand layer. The POU exit is situated above the sand layer, allowing the sand layer to be saturated with water during the operation. This promotes microbial development, resulting in the formation of biofilm surrounding the filter medium and sand particles. Research has shown that BSF can reduce turbidity and remove *E. coli*. Souter (2003) discovered that a BSF can remove 98% of *E. coli*. In another investigation, BSF with 10% zero-valent iron removed more than 5 logs of rotavirus (Bradley, Straub, Maraccini, & Markazi, 2011). According to the findings, virus elimination was mostly due to sorption to the filter material. Anaerobic BSF with ferrous iron addition was also discovered to be capable of reducing arsenic contamination in water. These tests revealed that the filter medium affected the kind of pollutant removed by BSF as well as its ability to remove additional pollutants.

According to CDC, (2012), the downsides of Bio Sand Filtration are as follows:

- Low viral inactivation;
- The lack of post-filtration residual protection, which means that if water is filtered, there is a risk of contamination if water is poured into an open or dirty bucket;
- The lack of research to demonstrate the health effects;
- The bio-sand filter is heavy and difficult to transport; and
- The initial cost is high that makes scalability more difficult.

2.2.3.2.Bone char

The charring of bones produces bone-char filters. Charring can be accomplished in two ways: as calcinations, in which bones are heated in the presence of a constant flow of oxygen from the atmosphere, or as pyrolysis, in which no oxygen is available during the heating (Wanjiru, 2015). Organic carbon is converted to carbon dioxide through calcination, and in pyrolysis, organic carbon is converted to inorganic carbon, which persists in the bone char. Pyrolysed bones are often completely black, while calcined bones are brown-grey-white, depending on the amount of oxygen available and hence the degree of charring (Dahi & Bregnhøj, 1995). Pyrolysis needs a lot of fuel, which makes it more costly.

The bone char is largely composed of apatite II (hydroxyapatite) ($Ca_{10}(PO_4)_6(OH)_2$ and about 10% elemental carbon, with some carbonate resulting from the deposition of calcium oxide during the ashing process and eventual reaction with atmospheric CO_2 (Wanjiru, 2015). There are three ways to remove contaminants using bone char. For starters, species may be integrated into the hydroxyapatite lattice by substituting Ca or CO_3. Second, species may associate with reactive groups on the carbon or hydroxyapatite surfaces (Physisorption and Chemisorption). Finally, free phosphate may form stable compounds with contaminants, causing them to precipitate. Fluoride and heavy metals are effectively removed by bone-char filters.

Charring animal bones remove organic material from the bone structure, resulting in a greater specific surface area and increased adsorption capacity (Kaseva, 2006). For example, Medellin *et al.*, (2007) reported a specific surface area of 104 m^2 /g for their tested bone char. Bone char also possesses advantageous surface chemistry, with Brunson and Sabatini (2008) discovering that the points of zero charge (PZC) of bone char are close to 8.3. In solutions with pH values less than the PZC, the bone char surface has a positive charge, while in solutions with pH values larger than the PZC, it has a negative charge. As a result, a material with a high PZC will have a positive surface charge, which will attract negatively charged fluoride ions for fluoride removal in groundwater with pH values approaching neutral. Korir *et al.* (2009) observed that bone char filters may reduce fluoride concentrations in distilled water from 6 mg/L to 6.2 mg/L in Kenyan groundwater to less than 0.1 mg/L.

Despite its advantageous surface chemistry and fluoride removal effectiveness, bone char is not commonly accepted in some communities due to religious and cultural reasons or poor char production quality (Fawell *et al.*, 2006), prompting the development of alternate materials.

2.2.3.3.Membrane filtration

Membrane filtration is one of the most effective methods of treating drinking water. It acts as a barrier for pathogens, keeping them contained inside the water source. Membrane filters necessitate the application of an external force. Filters having predetermined pore sizes, such as carbon block filters, porous ceramics containing colloidal silver, reactive membranes, polymeric membranes, and fibre/cloth filters, are used in a membrane separation process (Chaurasia, Singh, & Chandra, 2017). Physical straining via a single porous surface or numerous pore-structured surfaces is used to physically remove and retain microorganisms by size exclusion. Some of these filters may also employ chemically active antimicrobial or bacteriostatic surfaces or chemical changes to induce organisms to become adsorbed to filter media surfaces, inactivate, or at the very least not reproduce (Waghmare & Arfin, 2015). Semi-permeable membranes are thin, non-porous or porous polymeric sheets with ceramic or metal content, as well as liquid or gas content. The membrane should not melt, degrade, or rupture (Seadar & Heneley, 2002).

According to Ezugbe & Sudesh, (2020), the short falls of membrane filtration are as follows:

- The processes are susceptible to membrane fouling, which results in a reduction in permeate flow.
- Expensive cleaning and regeneration programs may be required.
- Cross-flow feed's high flow rates can cause shear damage to shear sensitive materials. The cost of equipment might be too expensive.
- Membranes with a broad pore size distribution may emerge if the membrane production process is not accurately regulated, resulting in poor separation performance.
- Operation cast is high which makes it difficult to implement in rural settings.

Reverse osmosis and nano-filtration are the most often utilized membrane separation methods for water treatment (Waghmare & Arfin, 2015).

2.2.3.3.1. Reverse Osmosis (RO)

The reverse osmosis method is a type of membrane separation technology that has shown to be very efficient at removing fluoride and inactivating different microbes. It has an 85-95 per cent fluoride removal performance and has been recommended by the US-EPA as one of the best possible fluoride removal techniques (Dysart, 2008). Pressure is exerted to force-feed water through a semipermeable membrane, extracting dissolved solutes (including fluoride) by rejection by the membrane depending on particle size and electrical charges in the reverse osmosis method. The technique is a physical procedure that reverses natural osmosis by applying pressure to the localized side of a membrane to counteract osmotic pressure.

The reverse osmosis strategy also has the following drawbacks:

- The mechanism for rural water supply in developed countries is complex: it necessitates special facilities, a constant supply of electricity, and professional workers, many of which are typically unavailable in rural areas of developing countries (Dysart, 2008).
- Expensive in terms of money, service, and maintenance (Meenakshi *et al.*, 2006).
- The operation wastes a large amount of water (typically 10-35 per cent), which can affect freshwater supplies and any water-saving efforts (Salifu, *et al.*, 2013).
- The method also eliminates the majority of the ions present in the water, even though some are needed as important minerals for the human body (Dysart, 6).
- It is hard to dispose of the concentrate containing rejected contaminants (Meenakshi & Maheshwari, 2006).

2.2.3.3.2. Nano filtration (NF) membrane process

The key distinction between RO and NF is that NF pores are wider than RO pores as a result of which they give less resistance to the entry of both solvents and solutes. Low pressure and low energy are required for NF, and solute removal is slightly lower throughout, and flow is faster (Waghmare & Arfin, 2015). The NF membrane separation process results in an imperfect defluoridation of water and an optimum concentration of fluoride in water can be obtained by adjusting operating conditions. Diawara *et al.* (2011) discovered that the NF membrane had a fluorine retention rate of around 63.3 % and 71 % in various parts of Senegal.

The following are the system's advantages: high efficiency, no additives are used, it meets requirements over a wide pH range, incursion owing to the presence of other ions is not detected, and this procedure creates a major barrier to suspended solids, inorganic contaminants, organic micropollutants, pesticides, and microorganisms. The following are the process's drawbacks: In comparison to other defluoridation procedures, which is a highly costly operation that is susceptible to fouling, scaling, or membrane degradation and destroys all ions present in water, some of which are required to the normal production and subsequent remineralisation of treated water(Diawara, *et al*., 2011).

2.2.4. Combination (multi-barrier) treatment approaches

These are any of the aforementioned methods used in conjunction, either concurrently or sequentially, for water treatment. Coagulation/disinfection, medium filtration/disinfection, or medium filtration/membrane filtration are examples of combinations or multiple barriers (Sobsey *et al*., 2008). Some combination systems are commercial items that come in the shape of granules, powders, or tablets and contain chemical coagulants like iron or aluminium salt as well as disinfectants like chlorine (CDC, 2012). When these chemicals are introduced to water, they coagulate and flocculate contaminants, promoting quick and efficient sedimentation and inactivating bacteria with the chemical disinfectant (e.g. chlorine). To use these combined coagulant/flocculant/disinfectant products, they are added to the specified volumes of water, allowed to react for floc formation, usually with a short mix to promote coagulation-flocculation, then allowed to settle unmixed, and the clarified supernatant water is decanted, usually using a cloth or other fine-mesh medium, to strain the reacted water (Dodd, 2012). The recovered supernatant is kept for some time, usually, several tens of minutes, to allow for further chemical cleaning before use.

2.3. Aluminium Oxide

Aluminium oxide (Al_2O_3), commonly known as aluminium (III) oxide, is an effective fluoride adsorbent (Loganathan, *et al*., 2013).

2.3.1. Physical and chemical properties of aluminium oxide

The hard-soft-acid-base (HSAB) concept may be used to explain why aluminium oxide is a good fluoride adsorbent. F^- is considered a hard base, whereas $Al3^+$ is considered a hard acid. Because hard acids and bases attract each other according to the HSAB principle, $Al3^+$ has a strong affinity for F^- (Salifu, *et al*. 2013). Another important aspect determining an adsorbent's performance is its point of zero charge (pHPZC). At a pH of 7, Ghorai & Pant (2005) showed that thermally treated aluminium oxide, also known as activated alumina, removes the most fluoride. Alumino-fluoro compounds develop and are discharged into the product water when the pH falls below 7. Other ions appear to be favoured by activated alumina above a pH of 7.

Mulugeta, *et al.,* (2013) characterized AO and found that the elemental structure analysis showed that AO has the formula of $Al(OH)_{2.8}(SO_4)_{0.1}$, and characterization findings (SEM, FTIR, and TGA) showed that the AO contains SO_4. Al NMR spectra also showed that the bulk of Al is coordinated octahedrally to oxygen (Al_6O), with the remainder involving pentahedral (Al_5O) and tetrahedral (Al). The components of a solid phase of AO are summarized in Table 2. AO contains aluminium, sulphate, sodium, iron and other minor elements. The high fluoride removal capacity of AO is attributed to the presence of sulphate and iron. Sulphate that is associated with aluminium is responsible for the acidity of the AO which contributes to high fluoride uptake capacity.

Table 2: Composition of AO

	Concentration (mg/g)	Concentration (mmol/g)
Al	228	10.7
Mn	0.39	0.01
Na	31	1.35
SO_4	155	1.61
Fe	25	0.44
Surface area(m^2/g)		37.7
Density (g/cm^3)		2.39
PZC		9.57

Source: Mulugeta *et al*, (2013)

The density of AO was 2.39 g/cm^3 according to the density measurement data. When the pH of the solution fell below the PZC (9.57), the surface of AO became positively charged, allowing fluoride adsorption via electrostatic interaction between fluoride ions and adsorbent.

2.3.2. Synthesis of aluminium oxide

Aluminium oxide can be synthesized by various routes such as the sol-gel method, electro spinning as well as standard method (Nordell, 2011).

Chaurasia *et al*., (2017) used the sol-gel technique to prepare aluminium oxide. The basis for the production of Al_2O_3 was aluminium chloride ($AlCl_3$) in an acidic media (ethanol). NH_3 was the other reagent employed in this procedure. In this technique, a 0.1 molar solution of $AlCl_3$ in ethanol was created by adding ethanol to $AlCl_3$. To remove $AlCl_3$ from ethanol, magnetic stirring was used for around 30 minutes. Following that, a 28 per cent NH_3 solution was added to the mixture as it was constantly stirred at a continuous feed rate, resulting in gel formation. For 30 hours, the gel was allowed to grow at room temperature. The gel was then dried in an oven at 100oC for 24 hours. In the oven, the gel was calcined at 1200^oC for 2 hours. The calcined sample was next processed for 30 hours in a planetary ball mill to further reduce the size of the crystal.

Mahapatra *et al*., (2011) used electro spinning to create aluminium oxide. Polyvinylpyrrolidone (PVP) solution (10% wt) was made by dissolving PVP polymer powder in 100% ethanol while stirring continuously and vigorously. Aluminium acetate was used as an aluminium intermediate by combining barium acetate and aluminium sulphate in a saturated solution. The aluminium precursor sol was mixed with a previously prepared PVP/ethanol solution, and 1–2 drops of acetic acid were added. The polymer-to-aluminium precursor weight ratio was kept constant at 3:1. The resultant PVP–aluminium acetate solution was placed in a 3 mL plastic syringe with a metallic needle. Using the syringe pump, the polymer solution was transported to the needle tip, and the feed rate was maintained at 1.0 ml / h. The positive terminal of the variable high voltage (14 kV) power supply (Glassman, Japan) was connected to the metallic needle, while the negative terminal was linked to the grounded collector, which was covered with aluminium foil and served as the counter electrode. The distance between the needle's tip and the collection was kept constant at 10 cm. All tests were carried out at room temperature with reasonably moderate humidity (45–50%). Following electrospinning, the as-spun PVP / aluminium acetate composite fibres were calcined in air for 2 hours at higher temperatures ($1000\ ^0C$) at a heating rate of $20\ ^0C$ / min to yield pure Al_2O_3 nanofibers.

2.4. Fluoride and bacterial removal batch experiments

Batch tests are undertaken during water treatment studies to explore the influence of different parameters on water purification. Several studies have been done on fluoride and bacterial removal.

Wang *et al.*, (2009) did research in China to investigate the potential of nanoscale aluminium oxide hydroxide (nano-AlOOH) for fluoride removal. Several batch adsorption studies were carried out to discover the parameters that influence the adsorption process. The factors studied were contact time, initial fluoride concentration, adsorbent dose, solution pH, and co-existing anions. The data demonstrated that as the adsorbent dosage increased, so did the percentage of fluoride removal, owing to an increase in the availability of fluoride binding sites as the adsorbent dose increased. The adsorption of fluoride to -AlOOH was also shown to be pH-dependent. Fluoride adsorption improved with a rise in pH, reaching a limit of 96.7%% at pH 6.8, and then decreased with a further rise in pH. High efficiency in acidic media can be attributed to a constant increase in attractive powers, whilst poor efficiency in an alkaline medium can be attributed to repulsion (Mahramanlioglu M, Iand, & Bicer, 2002). To explore the effects of coexisting ions, anion-containing solutions (Cl^-, NO_3^-, HCO_3^-, $SO_4^{2-,}$ and PO_4^{3+}) were created at concentrations of 50, 100, 150, and 200 mg/L by dissolving the predicted quantity of their sodium salt in a 10 mg/L fluoride solution. The results revealed that there was no significant impact on sorption in the presence of Cl^- or NO_3^-, but defluoridation effectiveness reduced by 30% in the presence of 50 mg/L SO_4^{2-} or $PO_4^{3-,}$ with a further 50% drop when the concentration of SO_4^{2-} or PO_4^{3-} was raised to 200 mg/L. SO_4^{2-} showed a larger negative influence on fluoride adsorption, which might be ascribed to sorption in part. Phosphate might be explained by the fact that phosphate and fluoride ions competed for the same active sites. During the contact duration, it was discovered that fluoride adsorption was very quick in the first 30 minutes and then gradually grew to reach pseudo-equilibrium in around 6 hours.

In another study carried out in Ghana by (Salifu, *et al*., 2013) on the purification of groundwater using aluminium oxide coated with pumice particles (AOCP), with fluoride removal as the main focus, the parameters tested during the batch experiments were temperature, adsorbent dosage and pH. AOCP samples were calcined at temperatures between 200^0C and 1000^0C, in a muffle furnace for 2 h. Fluoride removal performance decreased when the temperature of the AOCP was raised. High-temperature exposure of AOCP is anticipated to have a detrimental effect on the quality and longevity of the Al coating on the pumice particles that culminated in the development of an AOCP, resulting in a reduction in the number of hard surface sites accessible for fluoride binding. The impact of AOCP dosage on fluoride removal was investigated using varied adsorbent weights (1–20 mg/L) and a fixed fluoride concentration of 9.5 0.2 mg/L. Fluoride reduction effectiveness increased from 55.7% to 97.8 % when the adsorbent dose increased from 1 to 20 g/L. This might be attributed to an increase in the number of F-binding active surface sites as a result of higher adsorbent doses. In this investigation, adsorption was also demonstrated to be pH-dependent. Fluoride adsorption to AOCP was investigated at pH values ranging from 3 to 11. Fluoride adsorption improved with increasing initial pH in the acidic pH range, reaching a maximum removal efficiency of 93.4% at first pH = 6 with a corresponding removal power of 93.4%. (0.43 mg/g) and subsequently decreasing with increasing initial pH.

Zewge (2015) conducted another study in Ethiopia utilizing a combination aluminium sulphate/hydroxide technique to remove fluoride from drinking water. The fluoride removal efficiency was tested in batch testing as a function of adsorbent dose, contact duration, starting fluoride concentration, and solution pH. The contact time was investigated by altering the time from 0 to 60 minutes. The effects of the initial fluoride concentration were investigated using fluoride concentrations ranging from 5 to 30 mg/L. By altering the pH solution from 4 to 10, the effect of pH on fluoride removal was investigated. The data demonstrated that increasing the adsorbent dose resulted in an improvement in fluoride removal efficiency. A large number of fluoride binding sites made accessible by the adsorbent dosage was linked to improved fluoride adsorption efficacy. On the initial fluoride concentration parameter, the efficacy of fluoride removal was shown to be high for lower starting fluoride concentrations. The removal effectiveness of alum / AO, on the other hand, decreased with increasing starting concentration for a given weight of alum / AO. On the contact time parameter, it was discovered that a contact time of 15 minutes with an initial fluoride content of less than 15 mg / L resulted in a significant rate of fluoride removal. This means that the desired contact duration is critical for fluoride removal since the elimination of increasingly concentrated solution gradually achieved equilibrium. On the pH parameter, the percentage of fluoride removal remained nearly constant within the pH range of 5–9. When the pH was less than 5.0 or greater than 9.0, removal effectiveness decreased considerably. The electrostatic repulsion of fluoride ions to the negatively charged surface of $Al\ (OH)_4^-$ and competition from disproportionate concentrations of hydroxide ions are two mechanisms that contribute to the reduction in fluoride loss at solution pH values greater than 9. Fluoride elimination was reduced in solutions with pH less than 5, owing to electrostatic repulsion or the combined impact of chemical and electrostatic interactions between the flocculated surface and the fluoride ion.

Erkmen, (2010), studied antimicrobial effects of calcium hypochlorite on *E. coli* in water and selected vegetables. The effect of dosage, pH, and temperature was studied. The influence of dosage was investigated by varying the concentration of hypochlorite from 0.25 to 0.5, 1.0, 10, and 50 mg/L. The effect of temperature was studied with (20^0C, 30^0C, and 40^0C) with 10 mg/L HOCl at pH 7.0. The effect of pH was studied with (8.0, 7.0, 6.0, and 5.0) with 10 mg/L HOCl at 30^0C with contact time ranging from 30 to 270 sec. The results of various HOCl concentrations in deionized water on *E. coli* at 30^0C (pH 7.0) indicated that 10 mg/L HOCl significantly ($p<0.05$) decreased viable *E. coli* after a very brief exposure (30 sec), while 0.25 and 1.0 mg/L HOCl required exposure of over 1 minute. After a 30- second's exposure, the initial E. coli number was decreased by 2.54, 3.33, 3.92, and 5.57 logs/mL with 0.25, 0.5, 1.0, 10, and 50 mg/L HOCl, respectively, while a 6-log reduction was reached in 120 seconds with 10 and 50 mg/L HOCl. In 60 seconds, a chlorine concentration of 10 mg/L killed more than 5.66 log CFU/mL of E. coli. The effects of 10 mg/L HOCl (pH 7.0) in deionized water at different temperatures (20^0C, 30^0C, and 40^0C) on *E. coli*. The effects of temperature on *E. coli* inactivation using HOCl showed that the biocidal activity of chlorine decreases with decreasing temperature. *E. coli* was reduced by 3.57, 4.87, and 6.33 log CFU/mL after 30 sec at 20^0C, 30^0C, and 40^0C, respectively. The effect of pH showed that the maximal activity of HOCl on *E. coli* was observed in acidic solution. The concentration of undissociated HOCl molecules correlates with HOCl activity. The increased microbicidal activity of HOCl may be attributed to its diffusion across microbial walls. The behaviour of any given HOCl system is calculated by the combined concentration of H^+ ions (pH) and total available chlorine, which generate HOCl molecules as soon as they are exhausted by the disinfection method.

Given all these batch studies, there is still a research gap in the combination of aluminium oxide and flocculant/disinfectant such as calcium hypochlorite and the evaluation of its efficacy in enhancing both microbial and chemical water quality. Research on this will help in bridging this gap.

2.5. Testing the composite on real water samples.

Upon finding the optimal conditions for any water treatment product, the product has to be checked on real water samples so that any guidelines can be focused on real water samples (WHO, 2014). This is because the research technique has different physical, chemical and microbial properties than the real water samples.

In Tanzania, research was conducted by Kaseva, (2006) on the usage of mica clay material coated with aluminium oxide for fluoride removal. Batch studies were carried out using a homogenous combination of water containing 16 mg/L fluoride. Contact time, initial fluoride concentration, pH, adsorbent dose, particle size ranges, and temperature were all evaluated process factors. The findings revealed that the optimal pH was between 3-7.5, the optimal dosage was 8 g/L, and the contact duration was 30 minutes to reduce fluoride concentration to less than 1.5 mg/L. At an adsorbent particle size of 75 mm, the greatest percentage of adsorption was recorded. The optimal temperature was discovered to be greater than 600°C. Adsorbents' efficacy in removing fluoride was tested on actual water samples under controlled conditions. The average concentration of fluoride in all water samples obtained from eight water samples in Hai District was found to be 16 mg/L, which is above the WHO and Tanzania Bureau of Standards permissible limit (TBS). The water samples were treated with adsorbents. Fluoride concentration was decreased to 2.5 mg/L after treatment with activated mica, which is still above the safety limit. This was attributed to the alkalinity of the real water samples and the carbonate ions.

In Ethiopia, Zewge, (2015) performed research on defluoridation utilizing a combination aluminium sulphate/hydroxide method, and the method was tested on actual water samples from the Ethiopian Rift Valley after completing laboratory simulation conditions. The combined process efficiency for laboratory-prepared water samples was around % with an appropriate combined alum / AO dose (80 mg alum/mg F, 5 mg AO/mg F, and lime = 35 % alum). When the method was tested on real water samples from the Ethiopian Rift Valley, the best dosage was 90 mg alum/mg F, 5 mg AO/mg F, and 15% lime to achieve 85-93 % fluoride removal effectiveness.

In another study, Tully (2000) used calcium hypochlorite as a disinfectant of water. The experimental work involved the application of calcium hypochlorite to determine the amount of hypochlorite necessary to practically sterilize waters of different quality and the contact time required to sterile the water. Distilled water was contaminated with *E. coli* and the water was treated with different concentrations of calcium hypochlorite in the range of 0.1 to 50 mg/L. Samples were taken to count the number of viable CFU units for E. coli. 3 mg/L was considered as an optimum dose which achieved 5 $\log_{10}$ inactivation of E. coli and 30 minutes was considered as optimum contact time. When the conditions were applied on real samples from Lake Michigan, only 2 $\log_{10}$ inactivation of *E. coli* was achieved. This was attributed to the presence of organic matter in real water samples which increased chlorine demand and hence requiring high dose and more contact time.

From these studies, it has been shown that the water treatment conditions for the water prepared in the laboratory are different from the optimal conditions for the real water samples. It is therefore essential to test every water purification technology on real samples for proper recommendations.

2.6. Development of aluminium oxide (AO) based product

Aluminium oxide has received a lot of attention as a media coating for eliminating pollutants from water. Coating media improves its ability to remove dissolved contaminants such as fluoride and arsenic that the media would not be able to remove otherwise, while also retaining the media's filtration properties (Heidari, Moattar, Naseri, Samadi, & Khorasani, 2011). Salifu *et al*. (2013) coated pumice with aluminium oxide and reported a drop in fluoride content from 5 mg/L to 1.5 mg/L in one hour with an adsorbent concentration of 10 g/L. These batch adsorption studies were carried out at neutral pH, indicating that aluminium oxide coating may be used for drinking water purification. Zhao (2017) conducted research using aluminium oxide covered pumice using laboratory-scale BSFs. In this experiment, three BSFs were used: one with only sand, one with half covered pumice and half sand with the pumice layer on top, and one with coated pumice sandwiched between two layers of sand. Both filters with the aluminium oxide covering exhibited average residual fluoride concentrations of roughly 0.04 mg/L until they suffered breakthrough (Zhao 2017). Ganvir & Das (2011) used aluminium oxide-coated rice husk ash (RHA) to remove fluoride ions from drinking water. The coated RHA reduced fluoride levels from 20 mg/L to 1.2 mg/L, according to the results. Some plant adsorbents, such as bio char, pine sawdust, and activated carbon derived from bark, have been coated with aluminium oxide and shown to be more effective in removing fluoride.

According to the literature, aluminium oxide coating is effective in eliminating fluoride and should be investigated further for application in POU water treatment products. Different pollutants, such as bacteria, viruses, and arsenic, can also be eliminated concurrently with fluoride removal using aluminium oxide coatings.

3. MATERIALS AND METHODS

3.1. Synthesis of Aluminium Oxide (AO)

AO was synthesized using the recommended method (Mulugeta *et al.*, 2013). The precursor material was aluminium sulphate (alum). AO was prepared by mixing 100 g of $Al_2(SO_4)_3.14H_2O$ in 500 mL of distilled water while stirring with a magnetic stirrer until complete dissolution was achieved. 2M NaOH was used to adjust the pH. The precipitate (AO) was dried by exposure to sunlight. The AO was activated by heating it at a temperature of 300 ^oC in a furnace (Carbolite, ELF Model, UK) for 1 h. It was then thoroughly washed with deionized water to remove excess Na_2SO_4. The AO material was sun-dried again and crashed into powder with a mortar and pestle.

3.2. The batch experiments for fluoride and bacterial removal

3.2.1. Reagents and stock solutions

This study's chemicals and reagents were of analytical grade.

3.2.1.1. Fluoride solution

The fluoride stock solution was prepared by dissolving 2.21 g of anhydrous sodium fluoride in deionized water (99.0% NaF, BDH Chemicals Ltd, Poole, England) and filling up to 1000 mL with deionized water. The fluoride solutions used during the batch process were made by diluting the stock solution.

3.2.1.2. TISAB

Total Ionic strength adjustment buffer (TISAB) was prepared following the recommended procedure (Bailey, 1980), except that CDTA was substituted by EDTA as follows: 57 mL of glacial acetic acid, 58 g of sodium chloride, 7 g of sodium citrate and 2 g of EDTA was added to 500 mL of distilled water. After dissolution, the pH was adjusted to 5.3 using 5 M sodium hydroxide and then made up to 1 L in a volumetric flask with distilled water.

3.2.1.3. Chlorine stock solution

Because calcium hypochlorite is simple to store and contains 70% active chlorine, which lowers operating costs, it was chosen to produce a 1% chlorine stock solution. The chlorine solutions used during the batch process were made by diluting the stock solution. Equation 5 was used to compute the volume of chlorine stock solution required.

$$C_{Cl\,stock}V_{Cl\,stock} = C_{test\,water}V_{test\,water} \tag{5}$$

Where $C_{Cl\ stock}$ is the concentration of the stock solution, $V_{Cl\ stock}$ is the volume of stock solution $C_{test\ water}$ is the concentration of chlorine in test water V $_{test\ water}$ is the volume of test water

3.2.1.4. Nutrient agar

Preparation of MacConkey agar was done according to the manufacturer’s specification of dissolving 23 g of powdered nutrient agar in 1000 mL distilled water. This was followed by boiling to achieve complete dissolution. Then the suspension was sterilized by autoclaving for 15 minutes. Then, the agar was dispersed onto Petri dishes to prepare culture dishes.

3.2.1.5. *E. coli* stock culture

The Ethiopian Health and Nutrition Research Institute provided a permanent *E. coli* stock culture (EHNRI). Under sterile circumstances, an aliquot of the permanent stock culture was transferred to Petri dishes with sterile nutritional agar slants to create the working stock culture. These Petri dishes were grown overnight in a 37°C incubator. The Petri dishes were then placed in a 4°C freezer. The working stock culture was designed to last three weeks. The contents of the last two Petri dishes were utilized to establish a fresh collection of functional stock cultures.

Petri dishes containing sterile nutrient agar were inoculated with bacteria from the working stock culture to prepare them for inactivation tests. These Petri dishes were incubated at 37°C overnight. After washing with 10 mL of sterile distilled water and centrifuging for 10 minutes using a centrifuge, the bacteria were extracted. A vortex mixer was used to stir the microbial suspension at all times.

A determined amount of the *E. coli* stock culture was transferred to the test solutions for each experiment. By multiplying the required concentration of bacteria in the test solution by the volume of the test solution, the amount of stock culture to be added was estimated. The volume necessary was calculated using the formula below.

$$C_{E.coli\,stock}V_{E.coli\,stock} = C_{test\,water}V_{test\,water} \tag{6}$$

Where $C_{E.\ Coli}$ stock is the concentration of E. coli in the stock solution, $V_{E.coli}$ stock is the volume of E. coli stock solution, $C_{\text{test water}}$ is the concentration of E. coli required in test water and $V_{\text{test water}}$ is the volume of test water.

To prevent contamination, distilled water, all solutions, Petri dishes, beakers and pipette tips were autoclaved (121^0C for 15 min) before use. The working benches for all experiments were sterilized with 95% alcohol.

3.2.3. *E. coli* enumeration

The concentration of viable *E. coli* bacteria before and after treatment was determined using the pour plate method, as described in standard method 9215B (APHA, 2012). Dilution was used to reduce the concentration of the samples. To make test decimal dilutions, 1 mL of sample was added to pre-sterilized dilution tubes containing 9 mL of dilution water. The dilution tube that resulted held 10-1 mL of sample identical volume per mL of diluted sample. Using an aseptic approach, more decimal dilutions were made similarly. The plating dilutions were calculated based on predicted inactivation, with a goal of 30-300 colony-forming units (CFU) per plate.

Each set of experiments' Petri plates were made in duplicate and labelled accordingly. The culture plates were incubated for 24 to 25 hours at 370°C. At the end of the incubation period, the number of colonies was counted using a Quebec® colony counter. The following formula was applied in the *E. coli* count.

$$\boldsymbol{CFU/100\ mL = \frac{Average\ count}{Volume\ of\ the\ sample} * 100} \qquad (7)$$

Where CFU is the Colony Forming Unit

The removal efficiency of *E. coli* was expressed as $\log_{10}$ reduction value of bacteria using the following equation:

$$\mathbf{LRV = \log_{10}\frac{N_0}{N_t}} \qquad (8)$$

Where, LRV = log reduction value of bacteria count at time t; N_0 = initial bacterial concentration at time 0, N_t = final bacterial concentrations after a treatment time t.

The Log Reduction Values (LRV) can be converted to percentage efficiency by using the conversion factors as shown in Table 3.

Table 3: Conversion of LRV to percentage efficiency

LRV	Reduction (%)
1	90
2	99
3	99.9
4	99.99
5	99.999
6	99.9999

Source: Simonis & Basson, (2012).

3.2.4. Analysis of fluoride

A pH / ISE meter (Orion Model, EA 940 Expandable Ion Analyzer, USA) fitted with a combination ion selective fluoride electrode (Orion Model 96-09, USA) was used to measure the concentration of ion fluoride. The instrument was calibrated using standard solutions containing fluoride concentrations of 0.5, 1, 5, 10, and 20 mg/L before each trial. An equal volume of TISAB was added to each sample before measuring fluoride concentration. All samples were filtered through a 0.2μ m filter paper for fluoride analysis. All tests were carried out at room temperature. The fluoride removal percentage was determined as follows:

$$\% \boldsymbol{R} = \left(\frac{\boldsymbol{C_0} - \boldsymbol{C_t}}{\boldsymbol{C_0}}\right) \times \mathbf{100} \qquad (9)$$

Where, C_o and C_t are the initial and any time (t) fluoride concentrations in solution (mg/L), respectively.

3.2.5. Chlorine measurement

The concentration of chlorine and residual chorine was measured by the N, N-diethyl-*r*-phenylenediamine (DPD) method (Owoseni, *et al.*, 2017). Titration was carried out by filling the burette with FAS and its reading was recorded. Using a clean flask, 1 mL of DPD buffer and 1 mL of DPD indicator were added respectively to the sample. This was titrated against ferrous ammonium sulphate (FAS) solution until the pink colour just disappeared. The volume of FAS used was determined using burette readings before and after titration. The volume of FAS consumed during each titration was used to determine the chlorine concentrations in the solutions.

3.2.6. Batch tests

Batch experiments for fluoride removal and *E. coli* log reduction were carried out to optimize different experimental parameters such as contact time, initial fluoride concentration, dosage, initial *E. coli* concentration, and pH, all of which may influence fluoride removal and *E. coli* inactivation. All batch tests were performed in a 500 mL beaker containing 500 mL of fluoride spiking distilled water and *E. coli* under constant mixing conditions with a magnetic shaker at room temperature.

The sample solution(10 ml) was regularly removed from the beaker for fluoride and microbial analysis. All tests were conducted in triplicate and the mean values were used

3.2.6.1. Optimization of different parameters

Optimization of different parameters was done by studying one parameter at a time and keeping the remaining parameters constant.

3.2.6.1.1. Effect of dose

To study the effect of dose, experiments were conducted by varying doses of aluminium sulphate (700, 800, 900, 1000, and 1100 mg/L), AO (45, 75, 105, 135 and 165 mg/L) and lime (35% alum dose) at constant initial fluoride concentration of 15 mg/L and approximately 10^5 CFU/100 mL E. coli concentration. The dosage range was selected based on previous studies (Zewge, 2016). This was followed by the addition of calcium hypochlorite in the range of 0.5 to 4 mg/L to the optimum dose of alum, AO and lime. The choice of the different concentrations of calcium hypochlorite was based on the minimum and maximum limits set by WHO. The residual fluoride concentrations and *E. coli* concentrations were measured by taking samples after 1h. Chlorination was stopped with a quencher of 50 µL of 10% sodium thiosulphate.

3.2.6.1.2. Effect of contact time

The effect of contact time was studied by taking samples for analysis at different times from 10 to 120 minutes. All other parameters were kept constant (dose of 75 mg/L AO, alum 800 mg/L, 35% lime, 1.5 mg/L $CaOCl_2$, pH 6.7, initial fluoride concentration of 15mg/L and initial *E. coli* concentration of approximately 10^5 CFU/100 mL). Chlorination was stopped with a quencher of 50 µL of 10% sodium thiosulphate at different contact times.

3.2.6.1.3. Effect of Initial fluoride concentration

To study the effect of initial fluoride concentration, experiments were conducted by varying fluoride concentrations ranging from 5 to 30 mg/L at a pH of 6.7 and a constant dose of 75 mg/L AO, alum 800 mg/L, 1.5 mg/L $Ca(OCl)_2$, 35% lime, contact time of 30 minutes and initial *E. coli* concentration of 10^5 CFU/100 mL.

3.2.6.1.4. Effect of pH

The effect of raw water pH on fluoride removal and *E. coli* log reduction was investigated by varying the initial solution pH range from 3 to 10 at an initial fluoride concentration of 15 mg/L, a dose of 75 mg/L AO, alum 800 mg/L, $Ca(OCl)_2$, 35% lime, contact time of 30 minutes and initial *E. coli* concentration of 10^5 CFU/100 mL. 0.1 M NaOH and 0.1 M HCl were used to adjust pH to the desired level.

3.2.6.1.5. Effect of initial *E. coli* concentration

The effect of initial *E. coli* concentration was investigated by spiking the water with different *E. coli* concentrations (10^4, 10^5, 10^7, and 10^8 CFU/100 mL) at a constant fluoride concentration of 15 mg/L, contact time of 30 minutes, pH of 6.7 and a dose of 1.5 mg/L $Ca(OCl)_2$, 75 mg/L AO, 800 mg/L alum and 35% lime.

3.3. Testing the composite on real water samples

Real water samples were collected from different sites within the Ethiopian Rift Valley, Bora district (Tejitu, Dolessa, Tube), ATJK district (Germama, Galo Hirphe, Anano) and Dugda district (Serity, Wadesha) in 30-litre plastic Jeri cans, the samples for *E. coli* analysis were collected in sterilized bottles. The Jeri cans were labelled for identification before being properly stored and transferred to the laboratory. The dose of 1.5 mg/L $Ca(OCl)_2$, 75 mg/L AO, 800 mg/L alum and 35% lime was tested on these real water samples.

Water samples were analysed for different parameters before and after treatment. Methods of water quality analysis were done according to standard methods for the examination of water and wastewater specified by the American Public Health Association (APHA, 2005). The water samples were analysed for the following parameters; turbidity, pH, EC, fluoride, *E. coli*, alkalinity, sulphate, aluminium, residual chlorine and chloride. The values that were obtained were compared against the WHO drinking water standards to evaluate their suitability for drinking purposes.

3.4. Development of prototype household water purifier using aluminium oxide

Batch experiments were conducted to develop three POU prototype products as high dose, medium dose and low dose for treating water samples with ≤ 15 mg/L, ≤10 mg/L and ≤5 mg/L fluoride concentrations, respectively. The prototypes were developed using the optimum dose for effective fluoride removal and *E. coli* log reduction. The high dose prototype POU was developed using the dose of 95 mg/L AO, 900 mg/L alum, 15% lime and 2 mg/L $Ca(OCl)_{2.}$ The medium dose was developed using 85 mg/L AO, 850 mg/L alum, 15% lime and 2 mg/L $Ca(OCl)_2$. The low dose was developed using 75 mg/L AO, 800 mg/L alum, 15% lime and 2 mg/L $Ca(OCl)_2$. The chemicals were mixed and packed in a sachet. Finally, the chemicals were packed in a single sachet for POU water treatment. The instructions on how to use the product were printed and attached to the sachet. The amount of each sachet, the time required for treatment and the fluoride concentration are also included on the sachet.

3.5. Physico-chemical analysis of water treated with the prototype

The developed prototypes were tested on water samples from the Ethiopian Rift Valley. The contents were added in 10 litres of water and stirred for 5 minutes. Thereafter, water was allowed to settle for 25 minutes. After 25 minutes, water was filtered through a cloth and the filtered floc was disposed of. Water samples from Germama, Serity, and Galo Hirphe were treated with a high dose because the fluoride concentration was above 10 mg/L. Water samples from Tejitu and Anano were treated with a medium dose prototype. Water samples from Tube, Wadesha and Dollesa were treated with a low dose prototype. The treated water was analysed for turbidity, *E. coli*, aluminium, pH, chloride, sulphate, EC, fluoride, TDS, residual chlorine as well as alkalinity.

pH: Using a pH meter, the pH of the water samples was determined before and after treatment. The meter was calibrated with pH 4.0 and 7 standard buffer solutions. Before each reading, the electrode was thoroughly rinsed with distilled water. The tip was immersed in the sample until a consistent reading was obtained and recorded.

Conductivity: The conductivity of the samples was determined using a conductivity/TDS meter. To calibrate the meter, a standard conductivity solution of 12.88 mS/cm was used, and determining conductivity with the probe in the air was used as the zero point calibration. Before each reading, the probe was rinsed with distilled water. The conductivity readings were obtained by immersing the probe in the samples, covering it up to the indicated level, and waiting for a stable reading.

TDS: TDS was determined using a conductivity meter. The conductivity values were converted to TDS values by multiplying them by a conversion ratio factor of 0.5.

Turbidity: A turbidity meter was used to measure the turbidity of the water samples. The spectrophotometric turbidity meter was calibrated using turbidity 1 and 10 NTU standard solutions. Distilled water was also used to zero the meter. Water samples were placed in the provided glass bottles, which were then placed in the sample holders. Turbidity measurements were taken and recorded.

Alkalinity: The alkalinity of water was determined by titrating a water sample to pH = 4.5 with 0.1 N sulphuric acid. Phenolphthalein and methyl orange were the indicators that were used. The burette was filled with H_2SO_4 solution during the procedure. The sample was collected in a specific volume. Following that, 2-3 drops of phenolphthalein indicator were added. If the solution became pink, this indicated the presence of alkalinity, and it was titrated against H_2SO_4 until the pink colour disappeared. Following that, 1-2 drops of methyl orange indicator were added to the solution. The solution was titrated against H_2SO_4 until a light orange colour appeared. The total alkalinity was calculated using the following equation.

$$\boldsymbol{Total\ alkalinity = \frac{T*1000}{Volume\ of\ a\ sample}} \qquad (10)$$

Sulphate: Sulphate was measured using the nano color sulphate 200 or 1000 methods from Macherey-Nagel, GmbHA, using a UV-Vis spectrophotometer (Thermo Scientific Inc).

Aluminium and chloride: Aluminium and chloride were all measured using standard laboratory methods described by the APHA for the examination of water samples.

4. RESULTS AND DISCUSSION

4.1. Appearance of AO

The AO material looks brownish due to the presence of iron (Mulugeta *et al.*, 2014). Figure 13 in appendix 1 shows the appearance of AO.

4.2. The study of process parameters

The parameters such as contact time, initial fluoride concentration, pH, dosage, and initial *E. coli* concentration which affect the removal of fluoride ions and E. coli inactivation were studied by varying each of them at a time and keeping the remaining parameters constant. The results are presented below.

4.2.1. Effect of dose

Four chemicals were mixed to find the optimum dose, at a pH 6.7, initial fluoride concentration of 15 mg/L initial *E. coli* concentration of 10^5 CFU/100 mL and contact time of 60 minutes. The results are presented as fluoride removal efficiency and log $_{10}$ reduction of E. coli in Tables 4 and 6.

Table 4: Fluoride removal efficiency (%) for various combinations of alum, AO and 35% lime.

	Alum (mg/L)				
AO mg/L	700	800	900	1000	1100
45	83.2±0.71	85.7±0.81	90.1±0.08	91.2±0.07	92.1±0.45
75	85.8±0.43	92.1±0.51	93.2±0.56	93.9±0.73	94.1±0.18
105	87.1±0.63	92.5±0.54	92.9±0.54	94.1±1.12	94.9±0.38
135	89.7±0.71	93.1±0.87	93.7±0.76	94.5±0.34	95.2±0.41
165	90.7±0.98	94.7±0.53	94.8±0.34	95.1±0.28	95.7±0.37

Fluoride removal efficiency increased with rising dosage from 83.2% to 95.7%, as seen in Table 4. This is attributed to an increase in the production of higher amounts of precipitates and aluminium hydroxides which led to an increase in fluoride removal efficiency (Dargahi, *et al.*, 2016). There was no much improvement in the per cent fluoride removal at higher dosages than 75 mg/L AO and 800 mg/L alum owing to the presence of excess precipitates than that of fluoride ions, assuming that the amount of aluminium complex per fluoride ions stays constant. Higher alum/AO doses could lead to the wastage of chemicals without significantly increasing the amount of fluoride removed. This dosage of 75 mg/L AO, 800 mg/L alum and 35% lime is adequate to lower fluoride levels in drinking water to 1.5 mg/L, which is within the permissible WHO drinking water guideline. Similar results were obtained by Shimelis, *et al*., (2006) on the removal of fluoride from water using aluminium hydroxide. After a dose of 1.6 g/L, there was no significant change in fluoride removal hence that dose was considered the optimum dose

P-values from Anova at 95 % confidence interval for combinations of AO and alum was $4.4*10^{-59}$ as shown in Table 5 which is less than 0.05, meaning the difference in the means for the different combinations of AO and alum were statistically significant.

Table 5: Statistics for various combinations of alum, AO and 35% lime

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		
45 mg/L AO, 700 mg/L Alum	3	249.2	83.06667	0.023333		
45 mg/L AO, 800 mg/L Alum	3	256.2	85.4	0.04		
45 mg/L AO, 900 mg/L Alum	3	272.2	90.73333	0.323333		
45 mg/L AO, 1000 mg/L Alum	3	273.9	91.3	0.01		
45 mg/L AO, 1100 mg/L Alum	3	277.1	92.36667	0.093333		
75 mg/L AO,700 mg/L Alum	3	257.4	85.8	0.01		
75 mg/L AO , 800 mg/L Alum	3	276.6	92.2	0.01		
75 mg/L AO, 900 mg/L Alum	3	279.7	93.23333	0.063333		
75 mg/L AO, 1000 mg/L Alum	3	281.7	93.9	0.01		
75 mg/L AO, 1100 mg/L Alum	3	282.4	94.13333	0.003333		
105 mg/L AO,700 mg/L Alum	3	262.3	87.43333	0.063333		
105 mg/L AO, 800 mg/L Alum	3	277.3	92.43333	0.023333		

105 mg/L AO, 900 mg/L Alum	3	278.4	92.8	0.01		
105 mg/L AO ,1000 mg/L Alum	3	283	94.33333	0.023333		
105 mg/L AO, 1100 mg/L Alum	3	284.5	94.83333	0.003333		
135 mg/L AO,700 mg/L Alum	3	269.1	89.7	0.01		
135 mg/L AO,800 mg/L Alum	3	279.4	93.13333	0.003333		
135 mg/L AO, 900 mg/L Alum	3	281.1	93.7	0.01		
135 mg/L AO, 1000 mg/L Alum	3	283.6	94.53333	0.013333		
135 mg/L AO,1100 mg/L Alum	3	285.6	95.2	0.0091		
165 mg/L AO,700 mg/L Alum	3	272	90.66667	0.013333		
165 mg/L AO,800 mg/L Alum	3	283.8	94.6	0.01		
165 mg/L AO,900 mg/L Alum	3	284.2	94.73333	0.023333		
165 mg/L AO,1000 mg/L Alum	3	285.5	95.16667	0.003333		
165 mg/L AO,1100 mg/L Alum	3	286.6	95.53333	0.043333		
ANOVA						
Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	820.5555	24	34.18981	1006.649	4.4E-59	1.73708
Within Groups	1.6982	50	0.033964			
Total	822.2537	74				

Table 6 shows the effect of various combinations of AO and alum on *E. coli* log reduction

Table 6: log$_{10}$ reduction for E. coli for various combinations of alum, AO and 35% lime.

	Alum (mg/L)				
AO (mg/L)	700	800	900	1000	1100
45	0.0021±0.0005	0.0024±0.0001	0.0029±0.0001	0.0033±0.0004	0.0040±0.0005
75	0.0031±0.0005	0.0041±0.0005	0.0051±0.0004	0.0068±0.0004	0.0060±0.0010
105	0.0035±0.0010	0.0052±0.0004	0.0056±0.0001	0.0059±0.0001	0.0061±0.0005
135	0.0040±0.0010	0.0067±0.0004	0.0072±0.0004	0.0083±0.0004	0.0087±0.0001
165	0.0060±0.0001	0.0073±0.0002	0.0008±0.0005	0.0090±0.0005	0.0091±0.0005

Table 6 shows that various combinations of AO and alum did not produce efficient *E. coli* log reduction. The various combinations only reduced *E. coli* in a range of 0.0021 to 0.0091 log which corresponds to 2% to 9 % *E. coli* removal. As such, a dose of 75 mg/L AO and 800 mg/L alum was selected to be used for further dose optimization with calcium hypochlorite.

The dose of 75 mg/L AO, 800 mg/L alum and 35% lime was combined with different concentrations of calcium hypochlorite in the range of 0.5 to 4 mg/L. The results on fluoride removal efficiency, *E. coli* log reduction and residual chlorine concentration are shown in Table 7.

Table 7: Fluoride removal efficiency (%) and *E. coli* log reduction with 75 mg/L AO, 800 mg/L alum, 35% lime and different concentrations of calcium hypochlorite at 15 mg/L of fluoride and 105 CFU/ml.

Concentration of $Ca(OCl)_2$ (mg/L)	Fluoride removal efficiency (%)	Log $_{10}$ reduction for *E. coli*	Residual Chlorine
0.5	94.31±0.06	1.0±0.07	0.09±0.04
1.0	95.11±0.09	2.7±0.05	0.12±0.03
1.5	95.32±0.27	5.0±0.50	0.48±0.10
2.0	96.56±0.13	6.0±0.05	0.60±0.06
2.5	96.71±0.11	6.1±0.10	0.92.±0.07
3.0	97.22±0.24	6.2±0.70	1.21±0.01
3.5	97.31±0.56	6.4±0.90	1.50±0.02
4.0	97.89±0.70	6.7±0.40	1.72±0.09

The results show that there was a slight increase in fluoride removal after the addition of calcium hypochlorite. The following reaction takes place when calcium hypochlorite is added to water:

$$\boldsymbol{Ca(OCl)_2 \rightarrow Ca^{2+} + 2Cl^- + 2OCl^-} \qquad (11)$$

The calcium ion in the solution reacts with fluoride to form calcium fluoride (CaF_2), according to the following equation:

$$\boldsymbol{Ca^{2+} + F^- \rightarrow CaF_2} \qquad (12)$$

Calcium fluoride is insoluble and is left like a precipitate. This contributes to fluoride removal via precipitation (Kagne, *et al*., 2008).

The mechanisms of action of calcium hypochlorite on bacteria have been widely investigated (Virto, *et al.*, 2005). Calcium hypochlorite disinfects water by an inactivation process that causes damage to the cell membrane and cell wall of E. coli (Mizozoe, Otaki, & Aikawa, 2019). After the addition of calcium hypochlorite to water, hypochlorous acid ($HOCl^-$) is formed. Proteins and peptidoglycan bound to the cell wall and the cell membrane are the initial points of attack for chlorine disinfection (Dodd, 2012). After the damage of the cell wall and membrane, $HOCl^-$ can penetrate the cell wall and reach the cytoplasm, followed by reactions with purine and pyrimidine bases of the nucleic acids, whereby thymidine, deoxy guanosine, and uridine monophosphate are preferred targets. There was an increase in log reduction for *E. coli* with an addition of calcium hypochlorite as shown in Table 7. An increase in the dose of calcium hypochlorite led to an increase in log $_{10}$ reduction of *E. coli*. A low concentration of calcium hypochlorite produces low HOCl concentrations. As a result, at low concentration, the microbial inactivation is low due to its inability to reach the cytoplasm and to cause damage to the DNA (Erkmen, 2010). That's why 0.5 mg/L of $Ca(OCl)_2$ only achieved 1 log $_{10}$ reduction (about 90%) of *E. coli*. In contrast, higher chlorine concentrations cause a larger impairment of the cell wall and membrane, enabling HOCl to penetrate the cell wall and to react with the nucleic acids. This results in high-level DNA damage to the bacterial cells, consequently impeding DNA amplification, even for short amplicons (Dodd, 2012). This is why 4 mg/L of $Ca(OCl)_2$ achieved a 6.7 log $_{10}$ (99.9999%) reduction of *E. coli*. These results are in agreement with a previous study by Owoseni, *et al*., (2017) on the survival of *E. coli* collected from secondary effluents of two wastewater treatment facilities in the Eastern Cape Province of South Africa in the presence of different chlorine concentrations was studied in this study. The bacteria log reduction ranged from 1 to 3.88 at low calcium hypochlorite concentrations (0.5 to 1.5 mg/L). At higher calcium hypochlorite concentrations (3 to 5 mg/L), the bacteria log reduction ranged from 6 to 7.3.

The concentration of residual chlorine was in the range of 0.09 to 1.72 mg/L. Residual chlorine is defined as the concentration of chlorine species present in water after the oxidant demand has been met (Symons, Bradley, & Cleveland, 2000). According to CDC (2018), the presence of residual chlorine in drinking water implies two things. Firstly, it indicates that initially, enough chlorine was added to the water to inactivate the bacteria and viruses that cause water-borne diseases and secondly it indicates that the water is protected against recontamination during transportation and storage at home. The level of free chlorine in drinking water correlates with the absence of most disease-causing organisms and hence serves as a measure of water portability. The WHO recommends that free chlorine residual range of 0.2-0.5 mg/L is maintained at all points in the water supply for locations with little risk of cholera or associated epidemics (WHO, 2011).

P-values from Anova at 95 % confidence interval for fluoride removal efficiency, *E. coli* log reduction and residual chlorine concentrations for combinations of 75 mg/LAO, 800 mg/L alum, 35 % lime and different concentrations of calcium hypochlorite alum were 7.53* 10^{-33}, 4.81*10^{-37} and 1.9* 10^{-26} which is less than 0.05, meaning the difference in the means for the different combinations of AO and alum were statistically significant.

Since 1.5 mg/L for calcium hypochlorite produced 5 log reduction for *E. coli*, which is a good performance, and the residual chlorine concentration was 0.48 mg/Las which is enough to protect water from recontamination and it is within the WHO permissible limits, therefore, the dose of 1.5 mg/L $Ca(OCl)_2$, 75 mg/L AO, 800 mg/L alum and 35% lime was selected as an optimum dose for further experiments.

4.2.2. Effect of contact time

The effect of contact time on fluoride removal efficiency and *E. coli* log reduction was investigated by varying it from 10 to 120 minutes while keeping other parameters constant**.** Figure 2 shows the effect of contact time on fluoride removal.

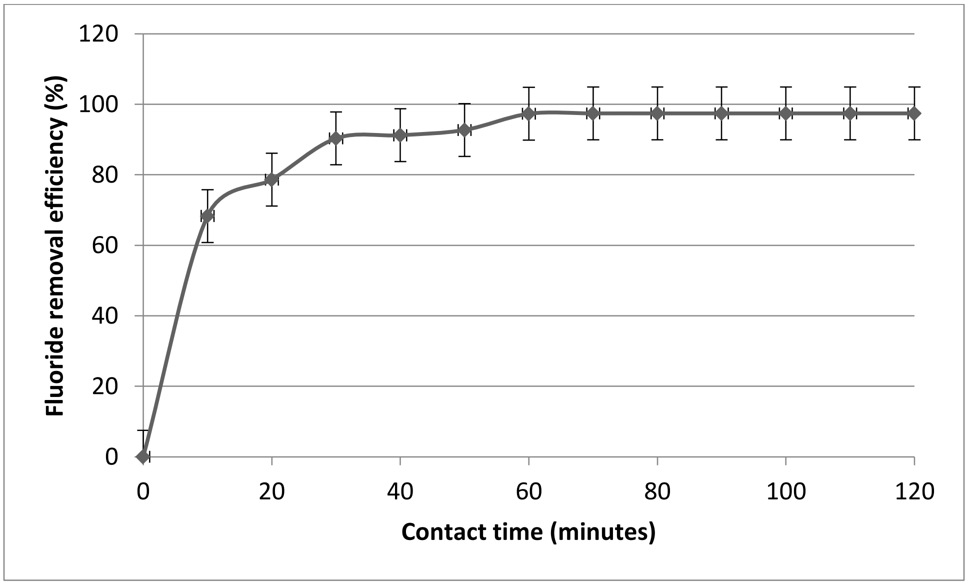

Figure 2: The effect of contact time on fluoride removal ([f] =15 mg/L, pH=6.7, E. coli =10^5 CFU/100ml, A0=75mg/L, alum=800mg/L, lime= 15% and $Ca(OCl)_2$=1.5mg/L)

Figure 4 shows that fluoride removal is fast within the first 15 minutes. Fluoride removal attains almost an equilibrium condition after 60 minutes. A contact time of 30 minutes is enough to remove 90 % of fluoride in a solution with the dose of 75 mg/L AO, 800 mg/L alum, 35% lime and 1.5 mg/L calcium hypochlorite. This shows that a contact time of more than 30 minutes does not have much effect on fluoride removal. Similar results were observed by Zewge (2015) for the removal of fluoride from water using a combined aluminium sulphate/ hydroxide process. The fluoride removal was fast within 15 minutes and 87.2 to 97.6% was achieved at an initial fluoride concentration of 15 mg/L with AO concentrations in the range of 45 to 300 mg/L and alum concentrations in the range of 900 to 1200 mg/L. A contact time of 15 minutes was selected as optimum for further experiments. Figure 3 shows the effect of contact time on *E. coli* log reduction.

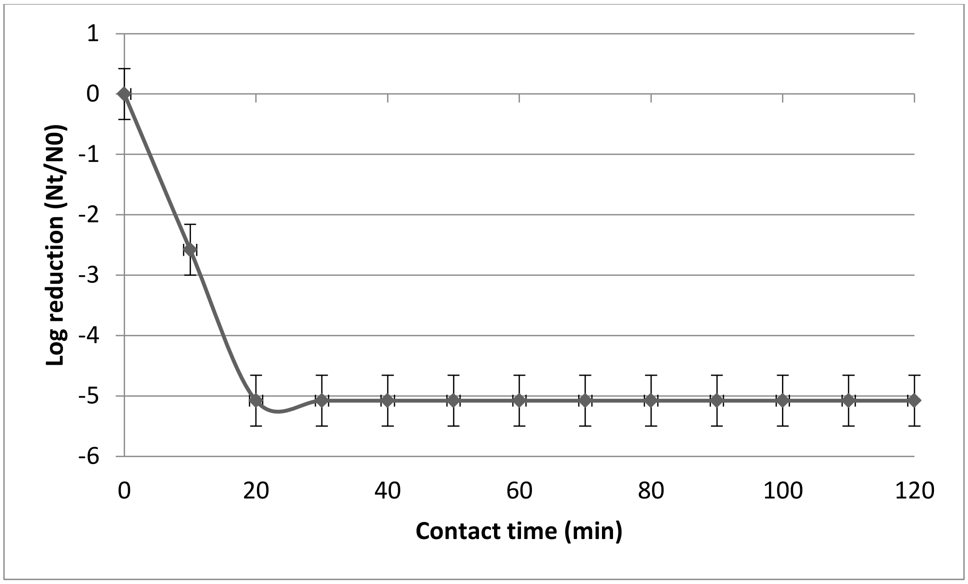

Figure 3: The effect of contact time on E. coli inactivation ([f] =15 mg/L, pH=6.7, E. coli =10^5 CFU/100ml, A0=75mg/L, alum=800mg/L, lime= 15% and Ca(OCl)$_2$=1.5mg/L)

Figure 5 shows that there was a 2.5 log $_{10}$ reduction of *E. coli* bacteria after 10 minutes of exposure. 5 log $_{10}$ reduction was achieved within 20 minutes. After 20 minutes there was no significant change in terms of *E. coli* log reduction. The results agree with previous research findings by Owoseni, Olanirani, & Okoh, (2017), on the inactivation of *E. coli* using calcium hypochlorite. The results showed that 5 log$_{10}$ E. coli reduction was achieved within 20 minutes and that after 20 minutes, there was no significant difference in *E. coli* log reduction. This shows that a contact time of more than 20 minutes does not affect E. coli inactivation.

Because the reactions involve *E. coli* log reduction and fluoride removal, and 30 minutes was enough to reduce fluoride concentrations to 1.5 mg/L and achieve 5 *E. coli* log reduction, a contact time of 30 minutes was selected as an optimum contact time for further experiments.

4.2.2.1.Effect of initial fluoride concentration

The effect of initial fluoride concentration on fluoride removal was investigated by varying the initial fluoride concentrations from 5 to 30 mg/L while maintaining other parameters (pH = 6. 7, contact time of 30 minutes, a dose of 75 mg/L AO, 800 mg/L alum, 35% lime, and 1.5 mg/L $Ca(OCl)_2$, and initial *E. coli* concentration of 10^5CFU/100 mL). The obtained findings were plotted as fluoride removal percentage versus initial concentration of fluoride (Figure 4) and *E. coli* log reduction versus initial fluoride concentration (Figure 5).

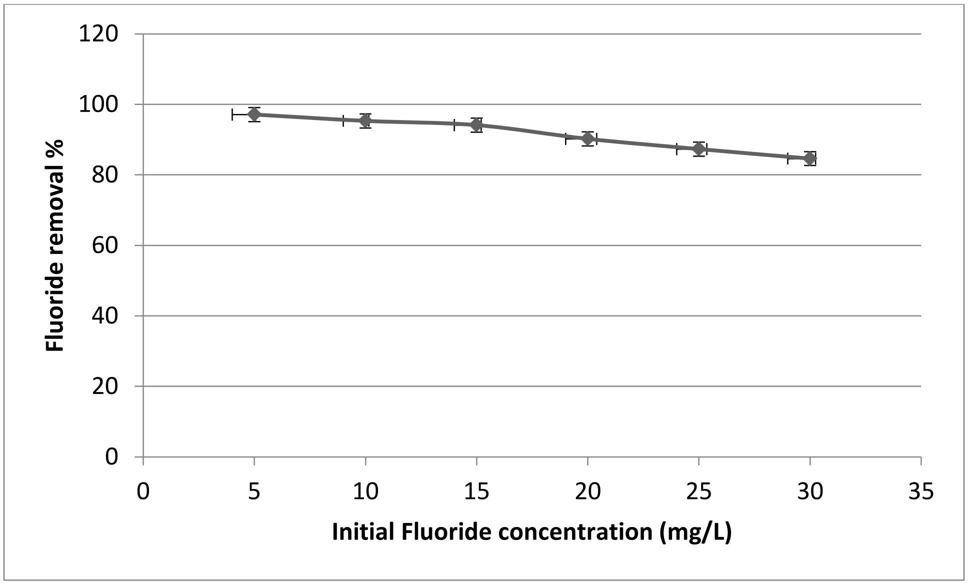

Figure 4: The effect of initial fluoride concentration on fluoride removal efficiency (contact time =15 minutes, pH=6.7, E. coli =10^5 CFU/100ml, A0=75mg/L, alum=800mg/L, lime= 15% and $Ca(OCl)_2$=1.5mg/L)

As shown in figure 4, maximum fluoride removal occurred at lower fluoride concentrations. For a given amount of coagulant level, fluoride removal is high at low fluoride concentrations because there are more aluminium oxide complexes for fluoride ions (Jagtap, *et al*., 2009). As fluoride concentrations increase, the binding potential of aluminium oxide reaches saturation, resulting in a decline in fluoride removal. This is attributed to the intensive use of all active sites on the complex's surface and incoming fluoride ion from the water was repelled by repulsive forces (Getachew, Hussein, & Rao, 2015). These results are in line with research by (Hussein & Vegi, 2020) who found that the fluoride removal efficiency reduced from 93% to 78% with the increase in initial fluoride concentration from 8 to 25 mg/L.

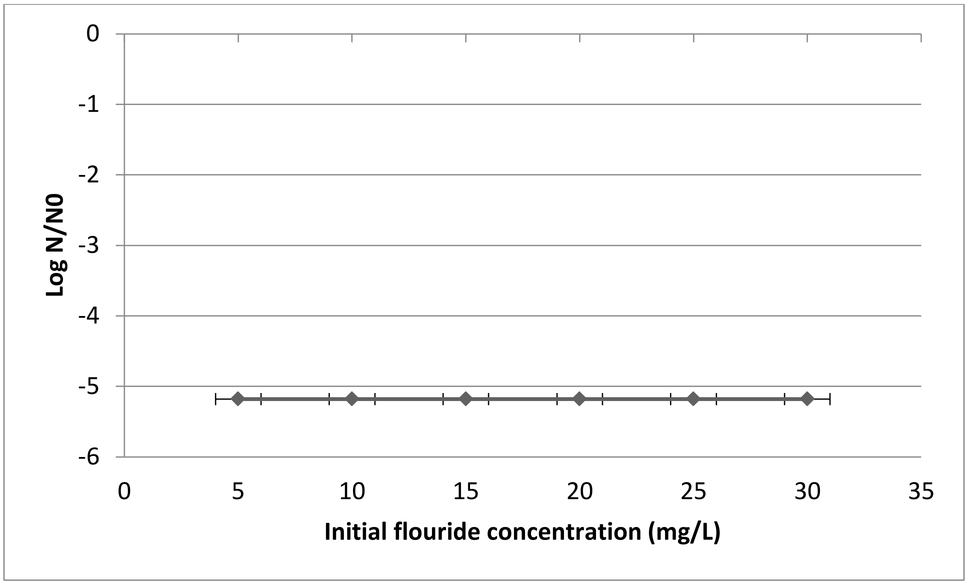

Figure 5: The effect of initial fluoride concentration on E. coli log reduction(contact time= 30 minutes, pH=6.7, E. coli =10^5 *CFU/100ml, A0=75mg/L, alum=800mg/L, lime= 15% and* $Ca(OCl)_2$*=1.5mg/L)*

As it can be seen from figure 5, initial fluoride concentration didn't have a significant effect on E. coli log reduction. Fluoride is toxic to bacteria, fungi, plants, and animals at high concentrations. Fluoride toxicity is thought to be caused in part by enzyme inhibition and interactions with important cations in the cell, such as Mg^{2+} and Ca^{2+} (Li, *et al.*, 2013). To overcome this problem of fluoride toxicity, *E. coli* bacteria developed fluoride resistance mechanisms. *E. coli* has a class of regulatory RNAs, or riboswitches, that bind to fluoride and regulate gene expression in response to this anion. Riboswitches are metabolite or ion-sensing structured RNA motifs that are typically found in the noncoding regions of specific mRNAs. They regulate the expression of neighbouring protein-coding regions via a variety of mechanisms, including transcription termination, translation blockade, and alternative splicing (Breaker, 2009). This explains why fluoride concentration did not affect *E. coli* log reduction.

4.2.3. Effect of pH

The pH of the solution is one of the important factors that affect fluoride removal and *E. coli* log reduction. The effect of pH was studied by varying it in the range of 3-10 while keeping all other parameters constant. Figures 6 and 7 depicts the effect of pH of the solution on fluoride removal efficiency and *E. coli* log reduction.

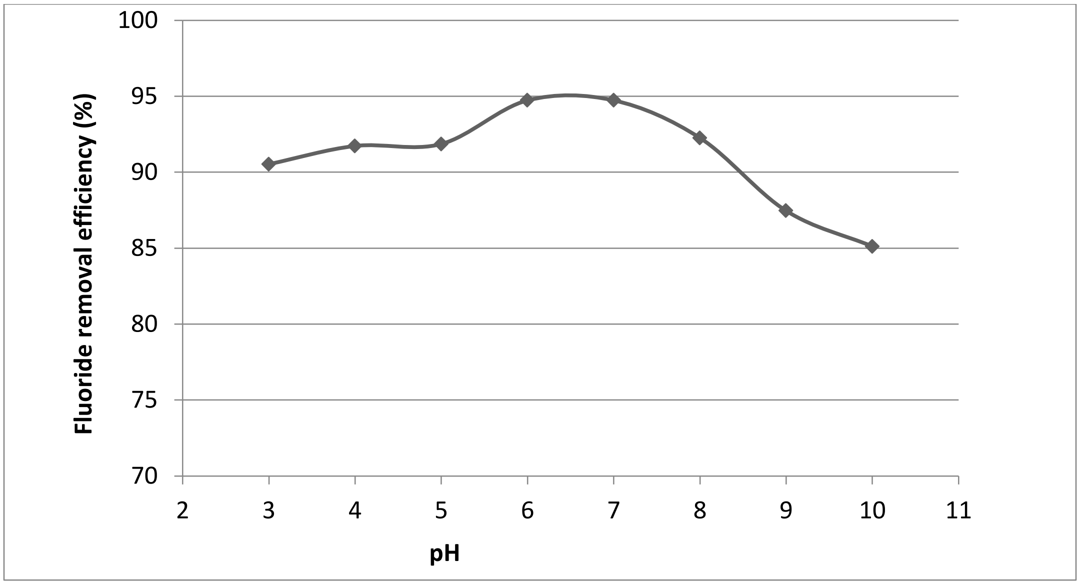

Figure 6: The effect of pH on fluoride removal ([f] =15 mg/L,contact time =15 minutes , E. coli =10^5 *CFU/100ml, A0=75mg/L, alum=800mg/L, lime= 15% and* $Ca(OCl)_2$*=1.5mg/L)*

The fluoride removal process which involves the hydrolysis of alum and the preferential adsorption of fluoride ions onto aluminium oxide that undergo precipitation is highly dependent on the pH of the solution. The pH affects the speciation of aluminium and it will have a significant influence on the defluoridation mechanism. The percentage of fluoride removal increases as the pH of the solution increases from 3 to 8 and the maximum fluoride removal is observed at pH 6- 7. $Al(OH)_3$ complex is responsible for fluoride removal. The $Al(OH)_3$ floc is believed to adsorb F^- strongly and the formation of this precipitate is optimal in a pH range of 6-7 (Aoudj, *et al*, 2012). Below the pH of 5, there is insufficient aluminium hydroxide precipitate

$Al(OH)_3$ since aluminium species such as Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ are prevalent (Hu, Lo, & Kaun, 2003). When the pH was raised to 10, the percentage of fluoride removal gradually decreased because soluble $Al(OH)_4^-$ is found to be the predominant species that repel the fluoride ions. This is consistent with the findings of Yang & Dluhy, (2002) who also found that the maximum fluoride removal using aluminium oxide was achieved with a pH range of 6 to 7.

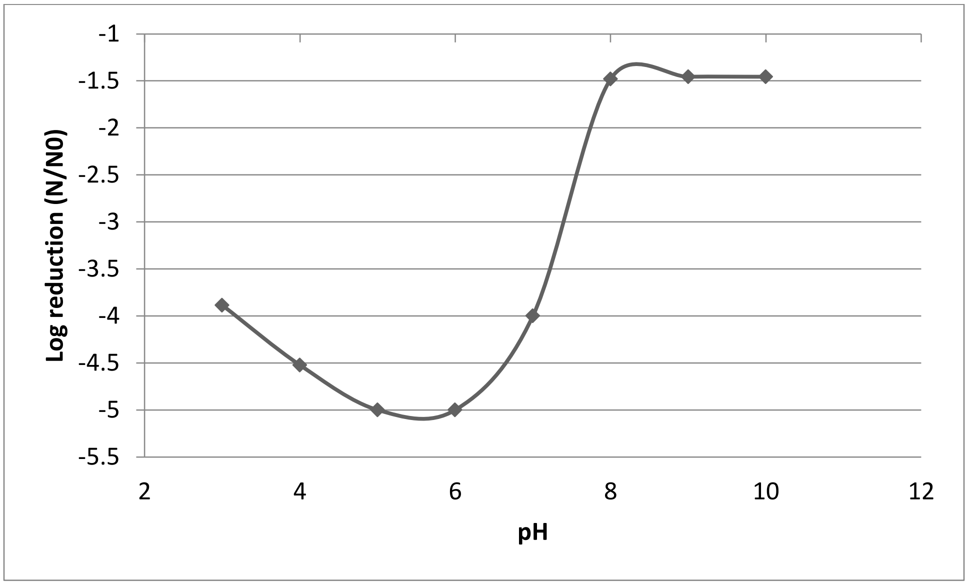

Figure 7: The effect of pH on E. coli log reduction([f] =15 mg/L, contact time =30 minutes, E. coli =10^5 CFU/100ml, A0=75mg/L, alum=800mg/L, lime= 15% and $Ca(OCl)_2$=1.5mg/L)

Figure 7 shows that the populations of *E. coli* were reduced by about 1 and 5 log 10 CFU/100 mL in a pH range of 3 to 10 with a maximum log reduction achieved at 5-6. pH is an important factor that influences the efficiency of the disinfection. When calcium hypochlorite is added to water, the following reaction takes place:

$$Ca(OCl)_2 + 2H_2O \rightarrow 2HOCl_{(aq)} + Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \qquad (13)$$

Hypochlorous acid dissociates to produce the hypochlorite ion as shown in the following equation:

$$HOCl \rightarrow H^+ + OCl^- \qquad (14)$$

Hypochlorous acid is more reactive than hypochlorite ion and a more powerful disinfectant and oxidant. The amount to which these reactions occur in water is determined by the solution's pH. As a result, the pH of a solution influences the quantities of HOCl and OCl^-. A higher pH allows the formation of more hypochlorite ions, resulting in less hypochlorous acid in the water. Lowering the pH allows for the formation of fewer hypochlorite ions and more hypochlorous acid. Hypochlorous acid is the most effective type of free chlorine residual, i.e., chlorine is accessible to kill microbes in water, whereas hypochlorite ions are far less effective disinfectants. As a result, disinfection is more efficient at low pH (with high amounts of hypochlorous acid in the water) than at high pH (with high amounts of hypochlorite ions in the water) (EPA, 2009). This explains why *E. coli* concentrations were lower in the acidic medium compared to basic media. These findings are consistent with those of Owoseni, Olanirani, & Okoh, (2017), who showed that maximal log reduction for *E. coli* with calcium hypochlorite was attained in pH solutions ranging from 3 to 7.

4.2.4. Effect of initial E. coli concentration

The effect of initial E. coli concentration on fluoride removal and *E. coli* log reduction was investigated by varying initial *E. coli* concentration in the range of $10^4 \pm 10$ to $10^8 \pm 20$ while keeping all other parameters constant. The results were plotted as the fluoride removal efficiency versus contact time and $\log_{10}$ reduction versus contact time. Figures 8 and 9 show the effect of initial *E. coli* concentration on fluoride removal and *E. coli* log reduction.

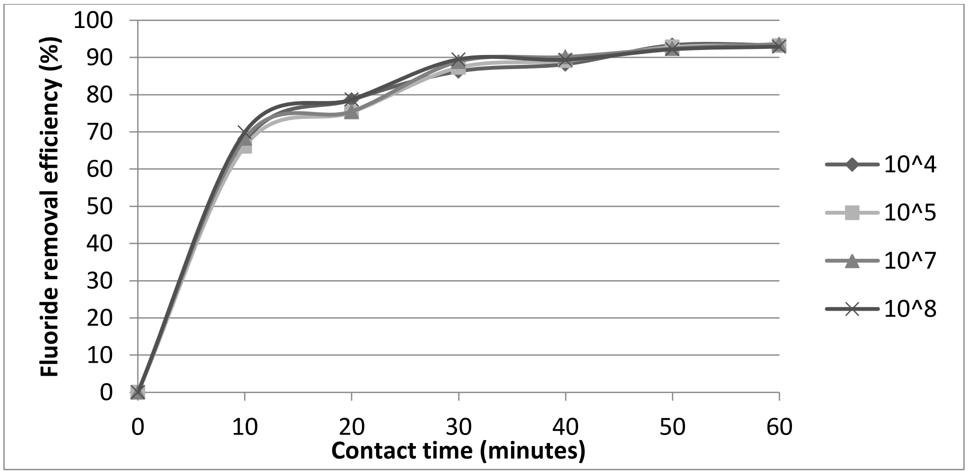

Figure 8: The effect of initial E. coli concentration on fluoride removal ([f] =15 mg/L, pH=6.7, A0=75mg/L, alum=800mg/L, lime= 15% and $Ca(OCl)_2$=1.5mg/L)

Figure 8 reveals that the initial *E. coli* concentration has no influence on fluoride removal. This might be attributed to the fact that there is no competition between *E. coli* and fluoride ions on the adsorbent site.

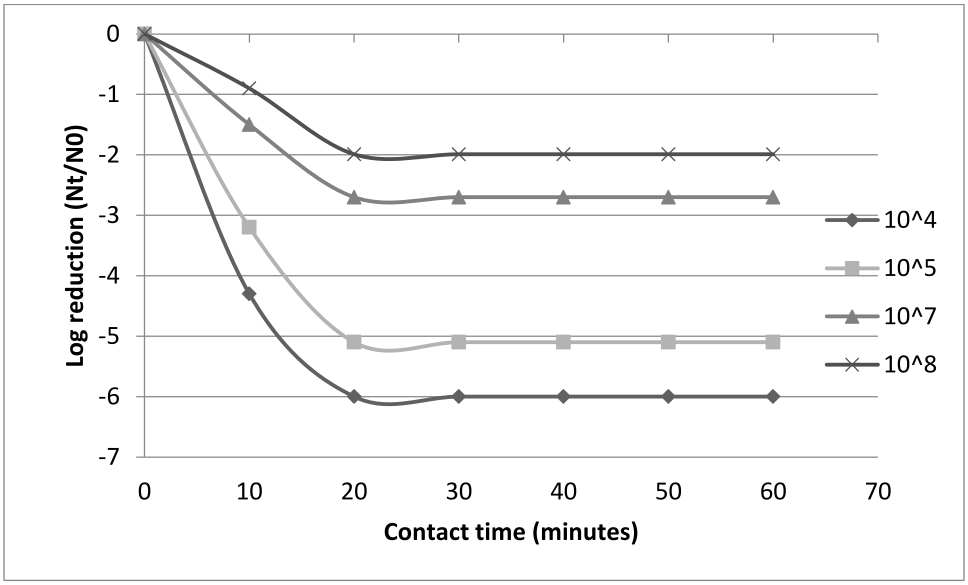

Figure 9: Effect of initial E. coli concentration on E. coli inactivation f] =15 mg/L, pH=6.7, A0=75mg/L, alum=800mg/L, lime= 15% and Ca(OCl)$_2$=1.5mg/L

Figure 9 shows that the log reduction rate decreased as *E. coli* concentration increased. At initial concentrations of 10^4 and 10^5 CFU/ 100 mL, 5 and 6 log $_{10}$ reduction was achieved. At initial concentrations of 10^7 and 10^8 CFU/mL, the reduction was reduced to log 2. To destroy the same proportion of *E. coli* cells at very high cell concentrations (10^8 CFU/100 mL and more), more calcium hypochlorite or longer treatment periods will be needed. The *E. coli* concentration-effect seen here may be attributed to the concentration of molecules available to interact with *E. coli* cells. To kill *E. coli*, there needs a direct interaction between a given concentration of hypochlorite in a solution and bacterial cell membranes (Owoseni, *et al*., 2017). This suggests that at high *E. coli* concentrations, a saturation point is reached where enough bioactive molecules are required to associate with main receptor locations within the cell. The concentration of hypochlorite ions available to kill *E. coli* cells become very limited at high *E. coli* concentrations and hence a higher reduction rate is not achieved (Erkmen, 2010). These results are in line with those of (Somolinos, *et al*., 2009) also claimed that initial *E. coli* concentration had an effect log inactivation of *E. coli*.

4.3.Testing the composite on real water samples

The dose of 1.5 mg/L $Ca(OCl)_2$, 75 mg/L, 800 mg/L alum and 35% lime was tested on the real water samples collected from the Ethiopian Rift Valley with a contact time of 30 minutes. Water samples were analysed for different parameters and compared with WHO as well as Ethiopian drinking water quality standards showed in appendix 1. The results are shown in Table 8.

Table 8: Concentrations of different water quality parameters of raw water (RW) and treated water (TW).

Drinking water quality parameters	Tube		Serity		Wadesha		Dollessa		Tejitu		Germama		Anano		Galo Hirphe	
Column1	RW	TW	RW	TW	RW	TW	RW	TW	RW	TW	RW	TW	RW	TW	RW	TW
Fluoride (mg/L)	3.67 ±0.10	0.4±0.01	12.3±0.34	1.6±0.08	4.33±0.56	0.70±0.01	5.55±0.23	0.97±0.12	9.63±0.31	1.63±0.03	15.1±0.09	2.8±0.03	10.5±0.24	2.36±0.67	12.6±0.21	2.64±0.12
pH	7.55 ±0.12	7.20±0.10	8.10±0.34	7.24±0.3	7.10±0.34	6.98 ± 0.50	8.19±0.40	6.62±0.20	8.10±0.12	7.32±0.01	8.01±0.45	7.16±0.01	7.66±0.82	6.90±0.01	7.71±0.23	7.13±0.12
EC(µs/cm)	410±0.79	546±0.50	770±0.90	836±1.50	560±1.20	710 ±2.00	530±1.03	767±1.00	700±1.33	836±2.00	1115±1.61	1335±1.50	1101±1.23	1348±1.50	1470±1.45	1720±2.00
TDS (mg/L)	205±1.22	273±1.50	385±1.72	458.5 ±0.50	280±1.92	355±1.21	265±2.33	383.5±2.16	350±1.21	418±1.50	557.5±1.83	667±1.50	550.5±0.21	674±2.00	735±1.21	8860±1.00
E. coli (Cfu/100ml)	$1.9*10^{5}$±13.0	19±2.12	$1.6 * 10^{5}$±10	0	$7*10^{4}$ ±19	0	$1.77*10^{5}$±21	0	$1.98*10^{5}$±23	0	$1.08*10^{5}$±17	87±4	$1.3*10^{4}$±12	0	$1.85*10^{5}$±21	0
Turbidity(NTU)	58±0.17	5±0.09	3.3±0.01	<1±0.01	10.1±0.31	<1±0.01	<1±0.03	<1±0.01	<1±0.01	<1±0.02	59±0.12	7±0.02	<1±0.01	<1±0.01	<1±0.01	<1±0.02
Alkalinity as CaCO3(mg/L)	739 ±0.81	-	821±0.91	-	-	-	856±0.12	-	809±0.21	-	791±0.21	-	784±0.01	-	836±0.12	
Aluminium (mg/L)	0.01 ±0.01	0.14±0.01	0.01±0.001	0.15±0.01	0.01±0.002	0.07±0.005	0.01±0.001	0.04±0.005	0.01±0.002	0.06±0.005	0.02±0.002	0.06±0.001	0.01±0.002	0.18±0.005	0.01±0.002	0.06±0.005
Chloride	1.19 ±0.01	2.35±0.10	1.20±0.12	3.10±0.05	0.47±0.03	1.30±0.01	0.40±0.03	1.27±0.20	0.90±0.21	2.10±0.20	1.43±0.02	3.97±0.08	0.82±0.02	2.70±0.10	1.39±0.21	4.10±0.10
Sulfate(mg/L)	87±0.89	135±1.00	98±0.91	140±1.50	45±0.11	61±1.50	50±0.70	117±1.50	67±0.45	127±1.00	56±2.12	97±1.50	30±0.21	73±0.50	75±0.21	117±1.00
Residual Chlorine (mg/L)	-	0.08±0.01	-	0.39±0.04	-	0.41±0.01	-	0.33±0.01	-	0.44±0.02	-	0.12±0.01	-	0.42±0.01	-	0.39±0.01

The fluoride removal efficiency was in the range of 78 to 89%. Treated water samples from Serity, Germama, Garlo Hirphe, Tejitu, Anano contained fluoride concentrations that were above the permissible drinking water standard as shown in Table 7. The reduced fluoride removal efficiency could be attributed to the alkalinity of the water samples. Alkalinity includes hydroxides, carbonates and bicarbonates. Carbonate has been shown to have a high affinity for $Al(OH)_3$. The observed decrease in fluoride removal may be attributed to rivalry for aluminium hydroxide complexes between the carbonates and fluoride anion (Aoudj, *et al*., 2012). A similar interfering role of alkalinity due to carbonate ion on fluoride removal by activated carbon was also reported by Meenakshi, *et al*., (2008).

Treated water from Tube and Germama had *E. coli* concentration which was above the WHO drinking water standard. Residual chlorine of these water samples was 0.08 and 0.12 mg/L respectively which is below both WHO and Ethiopian drinking water standards. This could be attributed to the turbidity of the water sample. The turbidity of these water samples was 58 NTU and 59 NTU for Tube and Germama, respectively. Turbidity contains organic compounds (Stange, Sidhu, Toze, & Tiehm, 2019). The organic compounds contained in turbidity are known to react with hypochlorite which increases the chlorine demand thereby reducing *E. coli* log reduction. In addition, organic and inorganic particles contained in turbidity protect microorganisms from free chlorine disinfection, a phenomenon recognized as 'particle association' (Ayyildiz, Ileria, & Sanikb, 2009). The stabilisation of cell membranes protects by restricting access to key components for cellular inactivation for microbial inactivation (Winward, Avery, Stephenson, & Jefferson, 2008). These results are in line with the findings by (Tangui, *et al*., 2019) where *E. coli* log reduction reduced from 4-log reduction to 1 log due to turbidity. It was discovered that total organic carbon interferes with the preservation of free chlorine residual. To preserve sufficient chlorine disinfection performance, turbidity of the raw water is suggested to be 1- 5 NTU or a high dose of coagulant and chlorine is required. The results show that the real water samples require a high dose of calcium hypochlorite to meet the drinking water standard for a turbid water sample.

Aluminium, chloride, sulphate, pH, alkalinity and total dissolved solids were within the permissible limits except for turbidity and electrical conductivity.

To meet the drinking water standards, batch experiments were conducted to find the dose that could effectively treat real water samples with high fluoride concentrations as well as high turbidity. The results showed that the water samples were alkaline and hence the lime dose was reduced. A dose of 85 mg/L AO, 850 mg/L alum, 2 mg/L and 15% lime effectively treated water samples with up to 10 mg/L while a dose of 85 mg/L AO, 900 mg/L alum, 15% lime and 2 mg/L calcium hypochlorite effectively treated real water samples which had up to 15 mg/L fluoride and 58 NTU turbidity.

4.4.Development of a prototype

The water purifier prototype was developed based on the results of the batch experiments conducted on real water samples. The real water samples contained fluoride concentrations in the range of 3.67 to 15.1 mg/L. Three different prototypes were developed to treat water that contains fluoride concentrations of ≤5, ≤10 and ≤15 mg/L. A dose of 75 mg/L AO, 800 mg/L alum, 2 mg/L $Ca(OCl)_2$ was used to develop a low dose prototype to treat water with fluoride concentrations of ≤5 mg/L. A dose of 85 mg/L AO, 850 mg/L alum, 2 mg/L and 15% lime was used to develop a medium dose prototype to treat water that contains fluoride concentrations of ≤10 mg/L. A dose of 95 mg/L AO, 900 mg/L alum, 15% lime and 2 mg/L was used to develop a high dose prototype to treat water that contains fluoride concentrations of ≤15mg/L. The high dose weighs 11.9 g and it contains 0.95 g AO, 9 g alum, 1.3 g lime and 2 mg/L active chlorine. The medium dose weighs 10.6 g and contains 0.85 g AO, 8.5 g alum, 1.27 g lime and 2 mg/L active chlorine. The low dose weighs 9.9 g and contains 0.75 g AO, 8 g alum, 1.2 g lime and 2 mg/L active chlorine.

Cost-plus pricing was used to approximate the cost of each sachet. Cost-based pricing is determining the overall expenses of producing your goods and then adding a percentage mark-up to establish the final price (Alberta Agriculture and Forestry, 2017). Approximately, each sachet would cost 2.00 Ethiopian birr. Figures 10 to 12 shows the three different POU prototypes along with instruction on how to use the sachets in Ahmaric.

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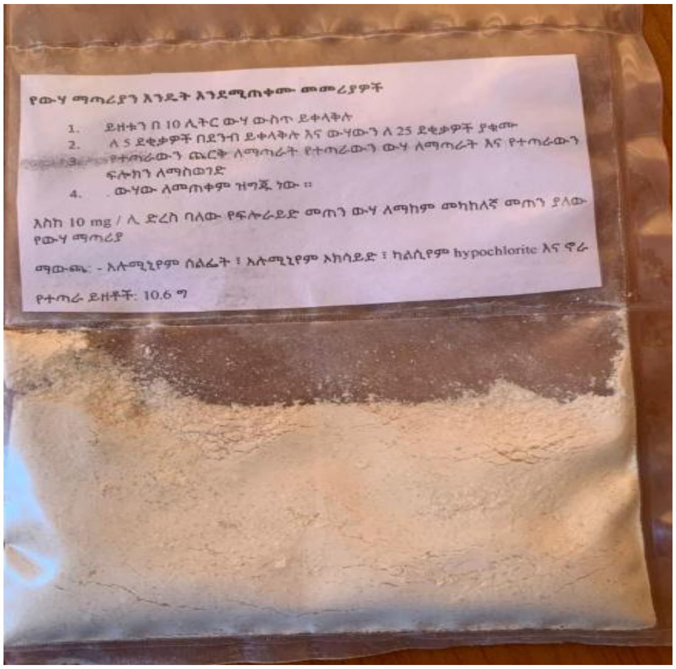
1. ይዘቱን በ 10 ሊትር ውሃ ውስጥ ይቀላቅሉ
2. ለ 5 ደቂቃዎች በደንብ ይቀላቅሉ እና ውሃውን ለ 25 ደቂቃዎች ያቁሙ
3. የተጣራውን ጨርቅ ለማጣራት የተጣራውን ውሃ ለማጣራት እና የተጣራውን ፍሎክን ለማስወገድ
4. . ውሃው ለመጠቀም ዝግጁ ነው ።

ውሃን እስከ 15 mg / ሊ. ድረስ ባለው የፍሎራይድ መጠን ለማከም ከፍተኛ መጠን ያለው የውሃ ማጣሪያ

ማውጫ: - አሉሚኒየም ሰልፌት ፣ አሉሚኒየም ኦክሳይድ ፣ ካልሲየም hypochlorite እና ኖራ

የተጣራ ይዘቶች: 11.9 ግ

Figure 10: A high dose water purifier prototype



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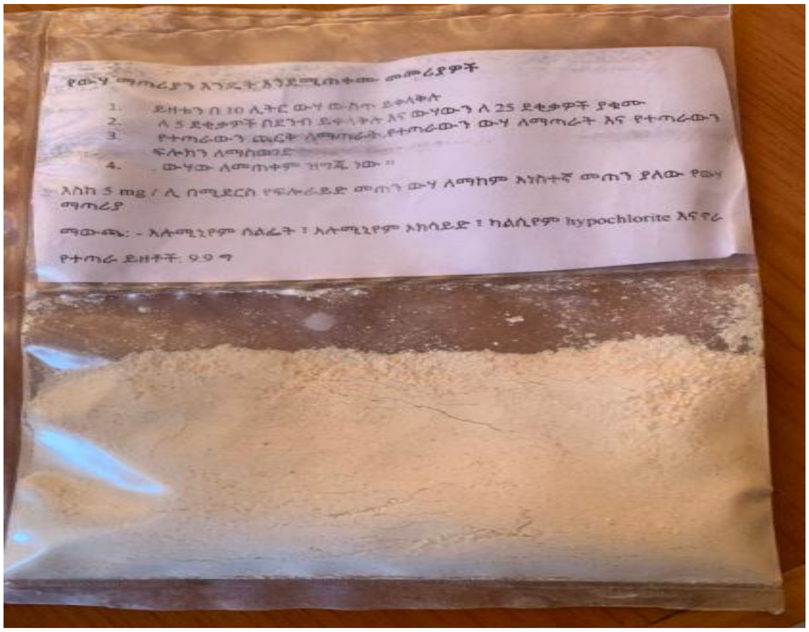
1. ይዘቱን በ 10 ሊትር ውሃ ውስጥ ይቀላቅሉ
2. ለ 5 ደቂቃዎች በደንብ ይቀላቅሉ እና ውሃውን ለ 25 ደቂቃዎች ያቁሙ
3. የተጣራውን ጨርቅ ለማጣራት የተጣራውን ውሃ ለማጣራት እና የተጣራውን ፍሎክን ለማስወገድ
4. . ውሃው ለመጠቀም ዝግጁ ነው ።

እስከ 10 mg / ሊ. ድረስ ባለው የፍሎራይድ መጠን ውሃ ለማከም መካከለኛ መጠን ያለው የውሃ ማጣሪያ

ማውጫ: - አሉሚኒየም ሰልፌት ፣ አሉሚኒየም ኦክሳይድ ፣ ካልሲየም hypochlorite እና ኖራ

የተጣራ ይዘቶች: 10.6 ግ

Figure 11: A Medium dose water purifier prototype



የውሃ ማጣሪያን እንዴት እንደሚጠቀሙ መመሪያዎች

1. ይዘቱን በ 10 ሊትር ውሃ ውስጥ ይቀላቅሉ
2. ለ 5 ደቂቃዎች በደንብ ይቀላቅሉ እና ውሃውን ለ 25 ደቂቃዎች ያቁሙ
3. የተጣራውን ጨርቅ ለማጣራት የተጣራውን ውሃ ለማጣራት እና የተጣራውን ፍሎክን ለማስወገድ
4. ውሃው ለመጠቀም ዝግጁ ነው ።

እስከ 5 mg / ሊ በሚደርስ የፍሎራይድ መጠን ውሃ ለማከም አነስተኛ መጠን ያለው የውሃ ማጣሪያ

ማውጫ: - አሉሚኒየም ሰልፌት ፣ አሉሚኒየም ኦክሳይድ ፣ ካልሲየም hypochlorite እና የሩ

የተጣራ ይዘቶች: 9.9 ግ

Figure 12: A low dose water purifier prototype

The prototypes were developed to be used as follows:

1. Mix the contents in 10 litres of water
2. Stir well for 5 minutes and let the water stand for 25 minutes
3. Use a clean cloth to filter the treated water and dispose of the filtered floc
4. The water is ready to use.

The product is should be stored in a cool dry place away from direct sunlight to avoid loss of active chlorine.

4.5. Physico-chemical analysis of water treated with the prototype

WHO established a set of standards for drinking water, with each parameter having a limit that must not be exceeded. However, each country has its drinking standards, which are mostly in line with the WHO standards. As a result, if the parameters exceed both limits, the water will be deemed unfit for human consumption.

The prototypes were tested on real water samples to assess their suitability for drinking purposes. Treated water was analysed for turbidity, *E. coli*, sulphate, alkalinity, aluminium, chloride, pH, EC, TDS as well as fluoride. Tables 9, 10 and 11 show the concentrations of different parameters of treated water using the high dose, medium dose and low dose POU prototype.

Table 9: Concentrations of drinking water parameters for raw water and treated water using the high dose POU prototype

Drinking water quality parameters	Germama		Serity		Galo Hiphe		WHO Standard
	RW	TW	RW	TW	RW	TW	
Fluoride (mg/L)	15.1±0.01	1.45±0.12	12.3±0.12	1.03±0.9	12.6±0.34	1.27±1.20	1.5
pH	8.01±0.16	7.12 ±0.05	8.1±0.23	7.11±0.05	8.00±0.45	7.09±0.01	6.5-9.5
EC(µs/cm)	1115±0.23	1410±0.70	770±0.26	920±1.20	1470±0.34	1810±1.30	1000
TDS (mg/L)	558±0.76	705±1.40	385±0.23	460±1.20	735±0.12	905±0.90	1000
E. coli	$1.08*10^{5}$±12	0	1.6 * 10^{5}±21	0	$1.85*10^{5}$±16	0	0
Turbidity	<1±0.01	<1±0.01	3.3±0.01	<1±0.01	<1±0.01	<1±0.02	<5
Alkalinity as CaCO3(mg/L)	841±1.23	-	831±0.47	-	836±0.34	-	250
Aluminium (mg/L)	0.02±0.01	0.1±0.01	0.01±0.001	0.18±0.02	0.01±0.001	0.08±0.002	0.05-2
Sulfate(mg/L)	56±0.92	107±0.15	98±0.72	133±0.93	75±0.34	132±0.73	250
Chloride	1.43±0.54	4.83±0.0	1.2±0.24	3.4±0.07	1.39±1.08	4.79±0.02	250
Residual chlorine	-	0.40±0.01	-	0.42±0.01	-	0.43±0.02	0.2-0.5

Table 10: Concentrations of drinking water parameters for raw and treated water using the medium-dose POU prototype

Drinking water quality parameters	Tejitu		Anano		WHO Standard
	RW	TW	RW	TW	
Fluoride (mg/L)	9.63±0.02	0.79±0.05	10.5±0.13	1.07±0.50	1.5
pH	8.1±0.30	7.12±0.01	8.2±0.12	6.89±0.50	6.5-9.5
EC(µs/cm)	700±0.19	911±1.50	1040±0.23	1270±1.20	1000
TDS (mg/L)	350±0.45	455.5±1.50	520±0.34	635±1.31	1000
E. coli (CFU/100 ml)	$1.98*10^5$±10	0	$1.3*10^4$±1	0	0
Turbidity (NTU)	<1±0.01	<1±0.01	<1±0.01	<1±0.01	<5
Alkalinity as CaCO3(mg/L)	809±0.21	-	784±0.021	-	250
Aluminium (mg/L)	0.01±0.001	0.1±0.005	0.01±0.001	0.2±0.003	0.05-2
Sulfate(mg/L)	67±0.45	109±1.2	30±0.21	97±1.3	250
Chloride(mg/L)	0.9±0.21	2.58±0.01	0.82±0.02	3±0.02	250
Residual chlorine (mg/L)	-	0.46±0.01	-	0.44±0.02	0.2-0.5

Table 11: Concentrations of water treated with a low dose POU prototype.

Drinking water quality parameters	Tube		Wadesha		Dollessa		WHO Standard
	RW	TW	RW	TW	RW	TW	
Fluoride (mg/L)	3.67±0.10	0.39±0.01	4.33±	0.42±0.03	5.55±0.32	0.79±0.15	1.5
pH	7.55±0.12	6.56±0.50	7.1±0.34	6.52±0.75	8.19±0.40	6.14±0.15	6.5-9.5
EC(μs/cm)	410±0.79	765±1.50	560±1.20	760±1.70	530±1.03	789±0.50	1000
TDS (mg/L)	205±1.22	382±1.50	280±1.92	380±1.30	265±2.33	394±0.9	1000
E. coli (CFU/100 ml)	$1.9*10^{5}\pm 13$	0	$7*10^{4}\pm 19$	0	$1.77*10^{5}\pm 21$	0	0
Turbidity (NTU)	58±0.43	2±0.01	10.1±0.21	<1±0.02	<1±0.01	<1±0.01	<5
Alkalinity as CaCO$_3$(mg/L)	739±0.81	-	-	-	856±0.12	-	200
Aluminium (mg/L)	0.01±0.001	0.16±0.003	0.01±0.001	0.20±0.02	0.01±0.001	0.07±0.001	0.05-2
Sulfate (mg/L)	87±0.89	147±1.50	45±0.11	77±1.20	50±0.70	118±0.9	250
Chloride (mg/L)	1.19 ±0.01	2.77±0.20	0.47±0.03	1.56±0.20	0.40±0.03	1.52±0.21	250
Residual chlorine (mg/L)	-	0.29±0.01	-	0.47±0.03	-	0.41±0.02	0.2-0.5

The pH of water is an extremely important indicator of water quality. It regulates metabolic processes in the body (WHO, 2011). The results show that the pH of the treated water is low than the raw water. This is because of the consumption of alkalinity due to coagulation. The pH of treated water for low dose, medium dose and high dose ranges between 6.14 to 7.12 which is within the acceptable WHO standards. These results are in line with the findings of

(Krupinska, 2020) who found that the pH of water treated with aluminium sulphate decreased from 7.47 to 7.12. The decrease in pH was attributed to the acid hydrolysis due to coagulation.

The treated water had elevated levels of conductivity. EC of the treated water ranged between 760 and 1810 µs/cm. Electrical conductivity is a measure of the ability of the water to conduct an electric current. EC was high in treated water because of cations and anions that were added in water after the dissolution of aluminium sulphate, aluminium oxide, calcium hypochlorite and lime (WHO, 2011). WHO set the EC standard as 1000 µs/cm so the treated water had the EC above the permissible limit. The results are in line with the findings of Miranda, Latour, & Blanco, (2020) who found that EC of treated water increased from 2100 µs/cm to 2500 µs/cm. This was attributed to the presence of monomeric and polymeric species after hydrolysis of aluminium ions.

Turbidity is a measure of how much water loses its transparency as a result of the presence of suspended particulates (Matta, 2014). The turbidity of the treated water was less than 5 which is within the acceptable drinking water standards. Turbidity was reduced in the treated water because alum flocculates suspended solids in the water together into large “fluffy” lumps. These lumps were settled making the water clear. Miranda, Latour & Blanco, (2020) also reported a decrease in turbidity from 198 to < 5 in water treated water with aluminium salts. This was attributed to the added coagulant (aluminium sulphate) which destabilizes the suspended contaminants which in turn make the particles contact each other and agglomerate thereby forming flocs.

Total dissolved solids for treated water was in the range of 380 to 905 mg/L which is high as compared to raw water which ranged 205 to 558 mg/L. The increase could be attributed to the addition of aluminium sulphate used to remove turbidity. As a result, more solids are dissolved in water. The values of TDS are within the permissible standards. The results are similar to research findings by Kumar & Balasundaram, (2017) who found that TDS of water treated with aluminium salts increased. This was attributed to the formation of sludge in the form of metal hydroxide together with coloured and colloidal matter that is removed from the raw water during treatment.

E. coli are bacteria found in people's and animals' intestines, as well as the environment. E. coli is a large and diverse bacterial group. Although the majority of E. coli strains are harmless, others can cause illness. Some E. coli strains can cause diarrhoea, while others can cause urinary tract infections; respiratory illness, pneumonia, and other illnesses (Jessoe, 2013). There were no *E. coli* colonies in treated water due to the successful treatment after the application of calcium hypochlorite. This complies with the drinking water standards for both WHO and Ethiopia.

The alkalinity of water is a measure of its ability to neutralize acids. Water alkalinity can be caused by the presence of one or more ions (WHO, 2011). Treated water did not contain alkalinity because of the addition of aluminium sulphate which removed the alkalinity. The alkalinity of treated water is within the WHO/Ethiopian permissible limit which is less than 200mg/L. The results are in line with the findings of (Krupinska, 2020) who indicated a decrease in alkalinity for water treated with aluminium sulphate. The decreased alkalinity was attributed to the hydrolysis of aluminium ions to form soluble monomeric and polymeric species and solid precipitates, which causes alkalinity consumption.

When an aluminium salt is used as a coagulation agent, a significant amount of aluminium is added to the raw water. The residual aluminium concentration, however, is closely related to the solubility of amorphous aluminium hydroxide at the actual pH after flocculation and filtration (EPA, 2009). Higher concentrations of aluminium in drinking water are linked to Alzheimer's disease. Aluminium for the treated water was in the range of 0.01-0.16 mg/L which is within the permissible WHO/Ethiopian standards. Krupinska, (2020) also found an increase in aluminium in water treated with aluminium sulphate. This was attributed to the hydrolysis of aluminium sulphate which increased aluminium polycations.

Sulphate is a naturally occurring sulphur and oxygen compound (WHO, 2011). Sulphate of the treated water was between 77 to 147 mg/L in treated water which is high than the raw water. The high concentration is attributed to the addition of aluminium sulphate which increased the concentration of sulphate ions in the treated water. The concentration of sulphate in treated water is within the permissible WHO/Ethiopian drinking water standards. The results are similar to the research findings by Yonge, (2012) who found that the concentration of sulphate in water treated by aluminium salts increased from 15mg/L to 113 mg /L. This was attributed to the hydrolysis of aluminium sulphate which increased the concentration of sulphate ions.

Chloride concentrations in treated water ranged from 1.52mg/L to 4.83 mg/L which is high than the concentration in raw water which ranged from 0.421mg/L to 1.43 mg/L. This could be attributed to the addition of calcium hypochlorite which increased the concentration of chloride ions in treated water.

Fluoride concentration in treated water was in the range of 0.24 mg/L to 1.27mg/L which is within the permissible WHO/Ethiopian drinking water standards.

Residual chlorine concentrations were in the range of 0.29 to 0.47 mg/L high which is within the recommended concentration. This means that the treated water will be protected against recontamination.

With the values of treated water of the mentioned parameters falling within the WHO and Ethiopian permissible limits, this means that the water is safe to drink and hence the product can be used for treating drinking water in rural settings.

5. CONCLUSIONS AND RECOMMENDATIONS

The study explored the development of a POU water treatment product that can reduce fluoride concentrations to within the permissible limits and improve microbial quality. Powder form water treatment prototype products were developed and their efficiency in treating drinking water was evaluated. Aluminium oxide, aluminium sulphate, calcium hypochlorite and lime were used in the development of the POU water treatment product. Aluminium oxide was prepared using a standard method.

Batch experiments were conducted to assess different factors that affect fluoride removal and E. coli inactivation. The results showed that the dose of 75 mg/L AO, 800 mg/L AO, 35% lime and 1.5 mg/L calcium hypochlorite effectively achieved 95% fluoride removal and 5 log $_{10}$ reduction of E. coli. A contact time of 30 minutes was found to be enough to achieve 90% fluoride removal and 5 log reduction of *E. coli*. Fluoride concentration showed to have an impact on fluoride removal as high fluoride concentrations resulted in reduced fluoride removal efficiency. On the other hand, fluoride concentration didn’t have any significant effect on *E. coli* log reduction. The pH of raw showed to have an impact on both fluoride removal and *E. coli* log reduction. Maximum fluoride removal was achieved at pH 6-7. Maximum *E. coli* log reduction was achieved at pH 6-7. Acidic pH values also achieved high log reduction. Initial *E. coli* concentration did not show any effect of fluoride removal but it showed an impact on *E. coli* log reduction.

The conditions of batch experiments performed on synthetic water in the laboratory were applied on real water samples collected from Ethiopian Rift Valley which had fluoride concentrations in the range of 3.67 to 15 .1 mg/L, *E. coli* concentration in the range of $1.98*10^5$ to $1.3*10^4$ CFU/100 mL and turbidity in the range of 58 to <1. The results showed that water samples from the Ethiopian Rift Valley required a high dose of alum, AO, calcium hypochlorite and a low dose of lime because of the alkalinity and because of the organic matter that is associated with turbidity. Batch experiments were conducted to find the conditions that were suitable for Rift Valley water samples. A dose of 75 mg/L AO, 800 mg/L alum, 2 mg/L active chlorine and 15% lime was used to develop a low dose water purifier which weighed 9.9 g for treating water samples with a fluoride concentration of ≤ 5 mg/L. A dose of 85 mg/L AO, 850 mg/L alum, 2 mg/L active chlorine and 15% lime was used to develop a medium dose water purifier that weighs 10.6g for treating water samples with a fluoride concentration of ≤ 10 mg/L. A dose of 95 mg/L AO, 900 mg/L alum, 2 mg/L active chlorine and 15% lime was used to develop a high dose water purifier that weighs 11.9 g for treating water samples with a fluoride concentration of ≤ 15 mg/L.

The POU prototypes were tested on water samples from Rift Valley. The treated was analysed for fluoride, turbidity, residual chlorine and chloride. The obtained values were compared with the WHO drinking water standards. All the parameters were within the permissible limits. The developed product effectively treated water with fluoride concentrations above 10 mg/L and turbidity above 5 NTU.

Based on the study, the following recommendations were made:

- Studies on the sensory evaluation of the product in terms of taste, odour, and colour need to be done.
- The concentrations of disinfection by-products need to be assessed.
- Since the POU prototypes were tested and found to be effective in improving water quality, communities lacking access to potable water should be encouraged to use them in drinking water treatment.
- The prototype should be tested at a pilot scale and upon its success, the product could be manufactured at a larger scale to which communities without access to portable water would use the product for treating drinking water at household scale up to commercial size. A cost analysis should be performed to assist in reducing additional costs and assessing the most reliable and cost-effective method of processing the POU.
- More research should be conducted on the POU prototype to determine its efficacy in eliminating other contaminants from drinking water such as arsenic, uranium and selenium.

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7. APPENDIX

Appendix 1: WHO and Ethiopian drinking water quality standards

Water quality parameter	WHO Standard	Ethiopian Standard
Fluoride (mg/L)	1.5	1.5
pH	6.5-9	6.5-8.5
EC (µs/cm)	1000	1000
Aluminium (mg/L)	0.05-2	0.2
Sulphate (mg/L)	250	250
Chloride (mg/L)	250	250
E. coli (CFU/100ml)	0	0
Turbidity (NTU)	5	5
Alkalinity (mg/L)	250	200
Total Dissolved solids (mg/L)	1000	1000
Residual chlorine(mg/l)	0.2-0.5	0.2-0.5

Source: (WHO/UNICEF, 2017; Bogale, 2020)

Appendix 2: Appearance of AO

Figure 13: Appearance of AO