UNIVERSITY OF CALIFORNIA

Los Angeles

Onsite Defluoridation Systems for Drinking Water Production

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Civil Engineering

by

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ABSTRACT OF THE DISSERTATION

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Doctor of Philosophy in Civil Engineering

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Fluoride in drinking water has several effects on the teeth and bones. At concentrations of 1-1.5 mg/L, fluoride can strengthen enamel, improving dental health, but at concentrations above 1.5 to 4 mg/L can cause dental fluorosis. At concentrations of 4 -10 mg/L, skeletal fluorosis can occur. There are many areas of the world that have excessive fluoride in drinking water, such as China, India, Sri Lanka, and the Rift Valley countries in Africa. Treatment solutions are needed, especially in poor areas where drinking water treatment plants are not available. On-site or individual treatment alternatives can be attractive if constructed from common materials and if simple enough to be constructed and maintained by users. This dissertation investigates using calcium carbonate as a cost effective sorbent for an onsite defluoridation drinking water system. Batch and column experiments were performed to characterize F^- removal properties. Fluoride sorption was described by Freundlich, Langmuir and Dubinin- Radushkevich isotherm models,

and it was found that the equilibrium time was approximately 3 hours, with approximately 77% of equilibrium concentration reached within 1 hour. Granular calcium carbonate was found to have comparable F^- removal abilities to the commercial ion exchange resins and possessed higher removal effectiveness compared to calcium containing eggshells and seashells. It was also found that the anion Cl- did not compete with F^- at typical drinking water concentrations, having little impact on the effectiveness of the treatment system. A fluoride removal system is proposed that can be used at home and can be maintained by users. Different calcium phosphate systems were also analyzed to find ways to improve fluoride removal rates. Adding phosphoric acid and calcium carbonate were effective in increasing fluoride removal rates. However, there would need to be a significant amount of phosphoric acid and initial pH would need to be approximately 1.5 or less to have optimal removal rates. We found the best results by using $Ca(OH)_2$ and NaH_2PO_4, with fluoride concentrations decreasing to 0.003 mg/L F^-. Through this work, we can be a step closer to bringing safe drinking water to those that do not have access to it.

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Dedication

This dissertation is dedicated to my family who has instilled in me the value of pursuing academics as one of the highest priorities in life. I want to thank my mom and dad for their utmost support in providing for me so that I could pursue higher education and helping me to get where I am today. I would also like to dedicate this dissertation to my husband for his support in helping me finish my dissertation and to my Christian family for praying for me. Lastly, but most importantly, I would like to thank God for helping me do what I cannot do on my own.

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1. INTRODUCTION

Since the 1990s, there have been great strides in providing safe drinking water sources to people around the world. 91 % of the world's population has access to improved (although not necessarily safe) drinking water sources in 2015 compared to 76% in 1990, an increase of approximately 2.6 billion people. More people have access to water through piped connections, public taps, protected wells and boreholes (WHO and UNICEF, 2015). However, there is still a great need to upgrade improved sources to safe drinking sources all around the world, in both the developed and developing countries. Approximately one-ninth of the people in the world still do not have access to a safe drinkable water source (UNICEF and WHO, 2012). One fourth of the population in developing countries lives under "acute water scarcity," such as in Asia. Two thirds of the people in Asia live without access to drinking water, and one half of the villages in India live with "acute drinking water shortage " (Gupta and Ayoob, 2016). At least 1.8 billion people drink from water sources contaminated with fecal matter and 663 million people drink from "unimproved" water sources, such as unprotected wells, surface water and streams. Approximately 319 million people are from Sub-Saharan African, 134 million people are from Southern Asia, 65 million from Eastern Asia and 61 million from South- Eastern Asia (WHO, 2016). Many developing countries also do not have the resources for a centralized water treatment system and the infrastructure to transport the water. Therefore, an alternative way to provide safe drinking water is needed and on-site water treatment systems that are simple, inexpensive and sustainable by the local population are attractive alternatives.

There are many contaminants in drinking water which can be divided into four categories: physical, chemical, biological and radiological. Physical contaminants are those that

affect the physical characteristics of water, such as sediments or organic material from soil erosion. Chemical contaminants are naturally occurring or manmade elements or compounds, such as nitrogen, metals, pharmaceuticals, salts, toxins, and pesticides. Biological contaminants are organisms in water, such as bacteria, viruses, protozoan and helminths. Radiological contaminants are unstable elements that have an unbalanced number of protons or neutrons, causing emission of radiation. Some examples are uranium, strontium, cesium, plutonium (EPA, 2016). In the United States, the top eleven causes of water contamination outbreaks in public water systems were : *Giardia*, *Legionella*, Norovirus, *Shigella*, *Campylobacter*, Copper, *Salmonella*, Hepatitis A, *Cryptosporidium*, *E. coli*, and excessive fluoride. The top thirteen causes of outbreaks in private water systems were: Hepatitis A, *Giardia*, *Campylobacter*, *Shigella*, *E. coli*, *Cryptosporidium*, *Salmonella*, Arsenic, Gasoline, Nitrate, Phenol, Selenium, *Yersinia enterocolitica* (CDC, 2014).

In this dissertation, we will be primarily focusing on excessive fluoride in drinking water as the contaminant of concern and the development of on-site defluoridation systems for drinking water production. The need for protection is established in the following chapters, followed by experiments to develop optimal treatment methods using calcium carbonate adsorption and calcium phosphate removal systems. The goal is to provide sustainable, easy to construct on-site treatment systems that will provide safe accessible drinking water to more people without the use of hazardous materials.

2. LITERATURE REVIEW

2.1 Background and Health Effects of Excessive Fluoride in Water

In limited quantities, fluoride is beneficial and essential to the mineralization of bones and strengthening of dental enamel, which is why it is added into US drinking water supplies, though this has been a controversy to this day (Adler et al., 1970; Carton, 2006). The safe limit of fluoride in drinking water is 1.0 mg/L in the U.S. and the recommended dose varies by location and climate. Forsman (1977) indicated that dental fluorosis probably wouldn't occur below a dosage of 0.1 mg F^-/ kg of body weight. The WHO guideline is 1.5 mg/L. It is known that fluoride levels of greater than 1.5 ppm cause fluorosis and adverse effects have been found from fluoride levels as low as 0.5 ppm (Ayoob, 2006). At concentrations from 1.5 to 4 mg/L, fluoride in drinking water can cause dental fluorosis. Gupta and Ayoob (2016) found that in Indian literature, there was a 100% occurrence of dental fluorosis at fluoride concentrations of 3.4-3.8 mg/L. At concentrations of 4 -10 mg/L, skeletal fluorosis can occur (WHO, 2004). A rough estimate from ASTDR states that a person that intakes 10-20 mg of fluoride per day for at least 10 years will get skeletal fluorosis (ATSDR, 2003). However, skeletal fluorosis has been found at low concentrations of 0.7 – 1.35 mg/L and crippling skeletal fluorosis has been found at concentrations of 2.8 mg/L. The incidence and severity of fluorosis varies between different locations with similar fluoride concentrations in drinking water, which shows that there are other factors affecting fluoride intake, such as fluoride in foodstuff (Ayoob and Gupta, 2016). Excessive fluoride in drinking water is a detrimental problem to society, causing detrimental effects to 35 nations across the world and putting 200 million people in the world at risk of fluorosis, both skeletal and dental (Jha et al., 2013; Gupta and Ayoob, 2016; MRD, 2004; Daw,

2004; Ayoob, 2008). Generally speaking, excessive fluoride causes stained teeth, bone diseases, tooth decay in the 1.5-4 mg/L fluoride concentration range and can develop to more serious conditions, such as skeletal fluorosis which causes stooped backs, and crooked hands and legs in the 4- 10 mg/L range leading to crippling skeletal fluorosis (Trikha and Sharma, 2014).

Crippling skeletal fluorosis is a severe form of skeletal fluorosis and is when kyphosis (curvature of the back causing hunchback), scoliosis (lateral curvature of the spine), *genu valgum* (one knee is angled in to touch the other knee) and *genu varum* (outward bowing of the knee), paraplegia (paralysis of lower body), and quadriplegia (paralysis of all four limbs) occurs (Gupta and Ayoob, 2016; Susheela, 2003). Paralysis occurs because of the increased size of the vertebrae bone as well as the narrowing of the spinal canal. The crippling deformities also cause neurological harm and auditory harm. Though total deafness is not likely, a decreasing ability to hear is observed because of a compression of the blood vessels affected by scoliosis and narrowing of the auditory canal (Ayoob and Gupta, 2006; Reddy et al., 2000; Rao and Siddiqui, 1962).

Fluoride can also lead to non-skeletal fluorosis, such as harmful effects to erythrocytes (red blood cells that transfer oxygen and carbon dioxide between tissues), ligaments, spermatozoa, thyroid glands (regulates rate of metabolism) and destruction of the actin and myosin filaments (motor proteins involved in muscle contractions) in the muscle tissues leading to muscle weakness and inability to do “routine activities” (Susheela, 2003). The gastrointestinal system is also adversely sensitive to fluoride in drinking water causing gastric irritation such as nausea, vomiting, and gastric pain (Spak, 1989). The gastric pain may be caused by the formation of hydrofluoric acid in the stomach (Susheela, 2003; Ayoob and Gupta, 2006;

Susheela, 1989). Fluoride can cause pathological changes such as DNA damage and lipid peroxidation (Wang et al., 2004). Further, excessive fluoride in water can lead to low hemoglobin levels, excessive thirst, frequent urination,“ tingling sensation in the fingers and toes”, headaches, skin rashes, depression, and negative neurological affects. It affects the brain tissues in a similar way to Alzheimer’s disease (Meenakshi and Maheshwari, 2006)
Studies have shown that children that intake excessive fluoride have lower IQ scores, “impaired cognition and memory,” and problems with “reaction response times and visuospatial capabilities,” especially when it comes to time sensitive tests (Trivedi et al., 2007; Wang et al., 2007; Calderon et al., 2000). There have been studies in India and China that have shown that children who drank water with higher fluoride concentrations ranging from 3- 5.55 mg/L F^- had significantly lower IQ scores than children who drank water with lower fluoride concentrations ranging from 0.37-2 mg/L (Lu et al., 2000; Trivedi et al., 2007; Aravind et al., 2016). We can suggest from these studies that neurological affects from fluoridated water can start occurring after 3 mg/L F^-.

Fluoride can also affect reproductive aspects in humans. There have been reported more “still and deformed childbirths” as well as decrease of birth rates in places with high fluoride concentrations. Fluorine can cause changes in the nervous system during pregnancy and can cross the blood brain barrier, accumulating in the brain tissue. This can cause disruption in “synthesis of receptors and neurotransmitters in the cells of the nervous system” (Gupta and Ayoob, 2015). Additionally, there seems to be a relationship between fluoride and the “morphology and mobility of sperm, levels of testosterone, and inhibin-B.” (Ozvath, 2009; Susheela and Jethanandani, 1996).

Excessive fluoride also affects the kidneys in detrimental ways because kidneys are the main organ that excretes the body of fluoride (Chandrajith et al., 2011). In children, intake of more than 2 mg/L of fluoride can damage liver and kidney functions. In India, in places with fluoride concentrations of 3.5-4.9 mg/L, people that had skeletal fluorosis were 4.6 times more likely to develop kidney stones (Singh et al., 2001). The lethal dose of sodium fluoride for a 70 kg person was found to be 5-10 g taken orally, which means 32-64 mg of fluoride/kg (Hodge and Smith, 1965). Any person who ingests more than that lethal dosage would be expected to die. People can be ingest fluoride from the food and beverages they intake. Table 2.1shows the fluoride concentrations found in a variety of food and beverages from around the world.

2.2 Genesis of Fluoride in Water and in our Bodies

Fluoride replaces the "hydroxyl and bicarbonate ions" that are associated with the minerals in your bone,

$Ca_5(PO_4)_3(OH)$, and form fluorapatite $Ca_5(PO_4)_3F$. This alters the mineral structure of bones, causing bones to be harder, denser and develop osteosclerosis, which is the hardening and "calcifying" of bones. This creates heavier more brittle bones that are more fragile than normal bones. Though fluorapatite has been used in medicine to increase bone mass, the "window" as to which this method is beneficial is small. The

Table 2.1. Fluoride concentrations found in a variety of food and beverages from around the world (Modified from Gupta and Ayoob, 2016).

Type of Food	Food Descriptions	Fluoride Concentration (mg/kg for solids; mg/L for liquid)	Study Area	References
Milk & Milk Products	30 samples of milk and milk products	0.23-1.36	Connersville and Richmond, Indiana, USA	Jackson et al., 2002
	66 milk samples	0.043-0.147	Tamil Nadu, India	Amalraj and Pius, 2013
	Soy beverages for infants	0.09-0.29	Bauru, Brazil	Buzalaf et al., 2004
Meat and poultry	9 kinds of deboned poultry meat	0.3-2.7	Poland	Jedra et al., 2001
	25 meats and chicken for infant	0.01-8.38	Iowa, USA	Heilman et al., 1997
Fish	bones of saltwater fish	45-1207	Camargo, Mexico	Camargo, 2003
	muscles of saltwater fish	1.3-26	Camargo, Mexico	Camargo, 2003
	3 different species of fish; water samples had 0.035-0.051 mg/L F-	2.35-274.29	Kerala, India	Thomas and James, 2013
Grains and Cereals	129 samples of grain products	0.07-1.36	Indiana, USA	Jackson et al., 2002
	66 cooked rice samples	0.34-0.73	Tamil Nadu, India	Amalraj and Pius, 2013
	cereals for infants	0.2-7.84	Bauru, Brazil	Buzalaf et al., 2004
	biscuits for infants	0.34-13.68	Bauru, Brazil	Buzalaf et al., 2004

Vegetables	65 samples of vegetables	0.38-5.37	Warsaw, Poland	Sawilska-Rautenstrauch et al., 1998
	660 leafy green vegetable samples	0.58-7.68	Tamil Nadu, India	Amalraj and Pius, 2013
	48 ready to eat samples of vegetables for infants	0.01-0.42	Iowa, USA	Heilman et al., 1997
Fruits and Juices	105 juice samples	0.67	Mexico City, Mexico	Jimenez- Farfan, 2004
	26 samples of fruits	0.01-0.84	Indiana, USA	Jackson et al., 2002
Sugars and Candy	15 samples of sweets and sugar	0.07-0.5	Indiana, USA	Jackson et al., 2002
Fats and Oils	14 samples of fats and oils	0.05-0.62	Indiana, USA	Jackson et al., 2002
Beverages	57 carbonated drinks	0.43	Mexico City, Mexico	Jimenez- Farfan, 2004
	332 samples of soft drinks	0.02-1.28	Iowa, USA	Heilman et al., 1999
Tea	6 kinds of tea	1.97-8.64	Taiwan	Lung et al., 2007
	Tea products	170-878	China	Wong et al., 2003
Bottled Drinking Water	10 types of bottled water	0.06-1.05	Davangere, India	Thippeswamy et al., 2010
	15 bottled waters (12 local and 3 imported brands)	0.5-0.83	Riyadh, Saudi Arabia	Aldrees and Al-Manea, 2010
	29 brands of bottled water	0.19-1.07	Algeria, Africa	Bengharez et al., 2012

same concept applies to our teeth and bones. Limited amounts of fluoride added to our teeth and bones forms fluorapatite and creates a strengthening effect, but after the "optimum" quantity of fluoride, too much hydroxyapatite converted to fluorapatite has detrimental health effects (Gupta and Ayoob, 2016; Nath and Dutta, 2015).

Fluoride gets into our groundwater when minerals and rocks containing fluoride go through dissolution or decomposition in the waters. This weathering of the rocks causes leaching of fluoride into groundwater. Some minerals that contain fluoride are: fluorite (~48 wt%), topaz (~11.5 wt%), fluorapatite (~3.8 wt%), biotite and muscovite (~1 wt%) , and rare minerals such as cryolite (~ 54 wt%) (Garcia and Borgnino, 2015). Additionally, rainwater becomes more acidic from CO_2 becoming carbonic acid. The carbonic acid comes from the soil and the atmosphere and also reactions between "bacteria and organic matter." Due to the acidity of the rainwater, salts in the soil, such as $NaHCO_3$, NaCl, Na_2SO_4, get "leached out" when rain percolates down the soil. Presence of sodium bicarbonates increases the dissolution of fluoride. Furthermore, phosphate fertilizers that are applied to the land usually contain fluoride, which increases fluoride concentrations in soil. Minerals and rocks containing $CaCO_3$ also get dissolved into the groundwater. Below are the mechanisms that happen: groundwater becomes more acidic with dissolution of CO_2 in water. Minerals from $CaCO_3$ get dissolved in groundwater forming fluorite CaF_2. When there are more sodium bicarbonates in groundwater, it reacts with CaF_2 and increases dissolution of fluoride in waters (Nair et al., 1984; Apambire et al., 1997; Salifu et al., 2012; Ibrahim et al., 1995; Gupta and Ayoob, 2016).

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad \text{Eq. (2.1)}$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad \text{Eq. (2.2)}$$

$$CaCO_3 + H^+ + 2F^- \rightarrow CaF_2 + HCO_3^- \qquad \text{Eq. (2.3)}$$

$$CaF_2 + 2NaHCO_3 \rightarrow CaCO_3 + 2F^- + H_2O + CO_2 \quad \text{Eq. (2.4)}$$

By looking at these equations, and the solubility product of $CaF_2 = [F^-]^2[Ca^{2+}] = 4* 10^{-11}$, it is clear that fluoride concentrations in waters are lower when calcium concentrations are high. Also, waters with high "sodium bicarbonate and bicarbonate chloride" usually have high fluoride concentrations (Gupta and Ayoob, 2016).

2.3 Locations in the World with Excessive Fluoride in Drinking Water

2.3.1 Fluoride in Water Due to Anthropogenic Reasons, Mountainous Regions with Marine Origins and Volcanic Activity

Groundwater is contaminated with fluoride due to anthropogenic and geological reasons. Fluoride can be released into the atmosphere and contaminate groundwater through several industrial processes, such as through cement and brick manufacturing, "coal fired power stations", electronics manufacturing, aluminum smelting and refining, beryllium abstraction plants, iron smelting and producing plants, "slag" processing using electric furnaces and steel manufacturing, phosphate fertilizer production and usage, glue production, etc. For example, an aluminum smelter plant in New South Wales, Australia had fluoride concentrations in their groundwater up to 3,000 mg/L F^- (Ramanathan, 2004; Nath and Dutta, 2010; Turner et al., 2005; Gupta and Ayoob, 2016).

Geologically speaking, fluoride occurs naturally in all waters. Seawater has around 1 mg/L of fluoride, and rivers and lakes usually have less than 0.5 mg/L (Fawell et al., 2006). Excessive fluoride can also be found in large geographical belts in mountains that have sediments of marine origins. An example of a geographical belt with marine origins is the mountainous regions from Afghanistan, Iraq and Iran to Syria and Turkey to Algeria and

Morocco. Other examples include southern parts of the USA, Europe, and USSR (Fawell et al., 2006; Gupta and Ayoob, 2016).

Furthermore, excessive fluoride can be found in geographical belts that have volcanic activity. The most well-known fluoride belt associated with volcanic activity is along the East African Rift from Eritrea to Malawi (WHO, 2005). The lakes in the Rift Valley system have fluoride concentrations of 1,640 mg/L in the Kenyan Lakes Elmentaita, 2,800 mg/L in the Nakuru Lakes and 690 mg/L in the Tanzanian Momella soda lakes (Nair *et al.,* 1984). Additionally, there are high concentrations in Naivasha, Mount Kenya, regions in the northern frontier, and "peri-urban areas of Nairobi" (Kaimenyi, 2004; Nair and Manji, 1982). In Tanzania, 8 to 12.7 mg/L of fluoride concentrations have been reported and severe fluorosis of all ranges has been reported in "Singida, Shinyanga, Mwanza, Kilimanjaro, Mara and Arusha regions." The disease has caused children to become immobile to do daily tasks. (Ayoob and Gupta, 2016; Mjengera and Mkongo, 2003). In "Dodoma, Kigoma, Tabora, and Tanga," people are only moderately affected by fluorosis. There is also high volcanic activity in the Nairobi, Rift Valley and Central Provinces with fluoride groundwater concentrations of 30-50 mg/L, especially in the Rift Valley with many instances of people with dental fluorosis and places with fluoride concentrations around 45 mg/L (Manji and Kapili, 1986; WHO, 2005). In the Ethiopian Central Rift Valley, an area extending from Syria and Jordan to Malawi and Mozambique, more than 40 % of the wells are contaminated with fluoride concentrations up to 26 mg/L F^- , especially in the deep wells with areas that have semi-arid climate (Tekle-Haimanot, R. et al., 2014).

2.3.2 Excessive Fluoride in Groundwater

Groundwater can also be contaminated with fluoride when it comes into contact with rocks and soils that naturally contain fluoride, such as fluorite, biotites, and topaz (Bhatnagur et al. 2011). Fluoride is leached into groundwater when the rocks decompose, dissociate and have long residence times in the groundwater (Nath and Dutta, 2010). Locations that have contaminated groundwater include Africa, China, Northern Thailand, Japan, Argentina, Persian Gulf, Saudi Arabia, Europe, USA, Canada, the Middle East, especially Pakistan, and southern Asia, especially India and Sri Lanka (WHO, 2005; Susheela,1995).

In China, people have been affected with dental and skeletal fluorosis since the 1990. In 1990, 300 million people had water with excessive fluoride concentration, 40 million were affected with dental fluorosis and 3 million people were affected with skeletal fluorosis. In 1995, it was reported that one tenth of the population suffered from fluorosis (Li and Cao, 1994). Endemic fluorosis has been observed in all 28 provinces except for Shanghai, especially those with deep groundwater. In the Kuitan region of Zhuiger basin, 26 million people suffered from dental fluorosis and 1 million people suffered from skeletal fluorosis, with a reported 21.5 mg/L concentration of fluoride. Excessive fluoride in drinking water was also reported in “Shanxi, Inner Mongolia, Shandong, Henan, and Xinjiang ”(Wang et al., 1997; Ayoob and Gupta, 2016). In 2006, it was reported that 21.45 million people suffer from dental fluorosis and 1.34 people suffer from skeletal fluorosis. In 2010, it was reported that there were 41.76 million cases of people who suffered from fluorosis in 1325 different counties in China. Of these cases, 58.2% were caused by excessive fluoride in drinking water (Fawell et al., 2006, WHO 2004, Wang and Huang, 1995; MHC, 2010; MHPRC, 2007).

In southern Africa, the North-West province, Limpopo, Northern Cape, and Kwa-Zulu-Natal provinces have been severely affected by excessive fluoride in groundwater (Ncube and

Schutte, 2004). In the North- West Province, 97% of the people are affected with dental fluorosis. In Western Bushveld and Pilanesberg, fluoride concentrations higher than 1 mg/L have been reported and up to 30 mg/L in alkaline waters with a pH higher than 9. 3, 0.48, and 0.19 mg/L of fluoride were reported in Lee Gamka, Kuboes, and Sanddrif respectively. Additionally, 95%, 50% and 47% of the school children in Lee Gamka, Kuboes, and Sanddrif respectively were affected by dental fluorosis (Coetzee et al., 2003; Grobler and Dreyer, 1988; Grobler et al., 2001; Mothusi,1998).

There is also groundwater contamination from excessive fluoride in Kenya, Ghana and Sudan. In Kenya, 44% to 77% of the people are affected by fluorosis, especially with those who drink waters from boreholes. A fluoride concentration of 18 mg/L has been reported. In a study of 1,000 groundwater samples, 600 of the samples exceeded 1 mg/L, 200 of the samples exceeded 5 mg/L and more than 150 samples exceeded 8 mg/L (Nair and Manji, 1982). In Ghana, 62% of the school children in the Bongo area drink from groundwater sources with excessive fluoride and have dental fluorosis. The water had levels of 0.11 to 4.6 mg/L of fluoride. In recent years, 11.6 mg/L of fluoride has been reported in the northern region of Ghana (Apambire et al., 1997, Salifu et al., 2012).In Sudan, in 1953, fluoride levels in groundwater were found in the range of 0.65-3.2 mg/L in Abu Deleig and Jebel Gaili. Dental fluorosis was prevalent for more than 60% of the population in Abu Deleig. In 1995, 91% of the children had dental fluorosis by just ingesting 0.25 mg/L of fluoride (Ibrahim et al., 1995; Smith and Smith, 1937; Ayoob and Gupta, 2006; Gupta and Ayoob, 2016).

In India, one half of the Indian villages are facing water shortages, partly because of the amount of groundwater used for food irrigation. In 2004, it was estimated that 3.7 billion bore wells were built for irrigation, which has caused pollution to groundwater sources and caused

"imbalance in the natural ecosystem." The pumping of groundwater has caused a decline in the "natural water table," which may have caused the entrance of pollutants, such as fluoride, into groundwater (Ayoob and Gupta, 2016).

Many places in India have high concentrations of fluoride. 20 out of the 32 states were found with high concentration of fluoride and a range of 0.5 to 70 mg/l of fluoride have been reported (UNICEF, 1999). 67 million people are "at risk" of fluorosis. The states with the highest levels of fluoride include: "Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh," with the highest concentrations found in the Rewari District of Haryana (48 mg/L), Rajasthan (69.7 mg/L), New Delhi (32 mg/L), and Assam (23 mg/L) (UNICEF, 1999; Gupta and Ayoob, 2016; Susheela, 2003). In the groundwater at Kurmapalli watershed in the Nalgonda district of Andhra Pradesh, a fluoride concentration of 21 mg/L was reported. The Nalgonda district is one of the worst affected states in India because of the "granite terrain" contaminating the groundwater. The granite rocks contain approximately 300 to 3,200 mg/L of fluoride, with a mean concentration of 1440 mg/L, which makes it the rock with the highest content of fluoride in the world (Mondal et al., 2009; Ramamohana Rao et al., 1993). In India, dental fluorosis has been reported at levels as low as 0.5 mg/L of fluoride, skeletal fluorosis at 0.7 mg/L, and crippling skeletal fluorosis at 2.8 mg/L (Ayoob et al., 2008; Agarwal et al., 1999; Ayoob and Gupta, 2006; Susheela and Bhatnagar, 1999).

High fluoride concentrations have been found in the United States' groundwater since the 1930s. In Colorado Springs, they first called the problem "mottled enamel" or "Colorado brown strain." In 1930, it was found that the fluoride in drinking water was the cause of the "mottled enamel" and the problem was renamed fluorosis. On January 25, 1945, a community's water supply was fluoridated in Grand Rapids, Michigan as a trial test (Lennon, 2006). Arnold et al.

(1956) published their results after 15 years of studying the community. They concluded that the total number of dental caries decreased by 50-63% in 12- 14 year olds and 48-50% in 15-16 year olds. In 1951, fluoridation of waters became an official policy of the US Public Health Service and by 1960 fluoridation of waters was widely applied for approximately 60 million people. In 2002, 46 out of 50 of US's largest cities had fluoridated water, with approximately 171 million people drinking from fluoridated waters. In 2006, 184 million people were drinking from fluoridated waters, which was approximately 61.5 % of the US population.

However, fluoridating public waters has been a controversy to this day. Carton, an environmental scientist (2006) who wrote regulations and performed research for the US Federal government for 30 years and the US EPA for 20 years, stated that he believed that the Maximum Contaminant Level Goal of 1 mg/L F^- started in 1985 by the EPA should be revised. He stated that the MCLG was based on only health effects known with "total certainty" and not "reasonably anticipated." He found that many negative health effects caused by fluoride in water, such as effects to the brain, endocrine, thyroid and joints etc., occurred at levels below 1 mg/L F^-, and urged that the new MCLG should be 0 mg/L (Carton, 2006).

Historically, defluoridation has been a need in several states affected by endemic fluorosis, such as "Arizona, Arkansas, California, Colorado, Idaho, Illinois, Iowa, Kansas, Minnesota, Nevada, New Mexico, North Carolina, North Dakota Oklahoma, Oregon, South Carolina, South Dakota, Texas, Utah and Virginia" (Dean, 1933). 1.06 to 4.07 mg/L of fluoride concentration was found in Illinois, and 0.3 to 4.3 mg/L of fluoride concentration was found in Texas (Segreto et al., 1984; Driscoll et al., 1983; Neuhold and Sigler, 1960). In the hot springs and geysers of Yellowstone National Park, fluoride concentrations of 25 to 50 mg/L were found. Furthermore, Lakeland, southern California had fluoride concentrations ranging from 3.6-5.3

mg/L (Cohen and Conrad, 1998; Fan et al., 2003) and Western United States had 5- 15 mg/L of fluoride found in their deep aquifers (Reardon and Wang, 2000; Gupta and Ayoob, 2016).

Recently, in the United States, it has been found that 35.4 % of the groundwater supplies in the six desert regions of southern California had high concentrations of at least one or more of the following contaminants: arsenic (17.8 %), boron (11.4%), fluoride (8.9 %), gross-alpha radioactivity (6.6%), molybdenum (5.7%), strontium (3.7 %), vanadium (3.6 %), uranium (3.2 %), and perchlorate (2.4 %). Out of the six desert regions, all of them had groundwater aquifers with high concentrations of fluoride except for Indian Wells, which had around 32% of the aquifers with moderate levels of fluoride. Approximately 22 % of the aquifers in Coachella Valley, 20 % in the Colorado River basin, 10% in the Mojave River area, 3 % in the Owens Valley and 3% in the Antelope Valley had high concentrations of fluoride (Dawson & Belitz, 2012). In the Coachella Valley, Owens Valley and Indian Wells, high and moderate fluoride concentrations were found in " upgradient and downgradient areas." In the Antelope Valley and Mojave River areas, high concentrations of fluoride were found "mostly in downgradient areas." In the Coachella Valley, high concentrations of fluoride were found in the "Needles and Palo Verdes basins and not in the Yuman basin" (Dawson and Belitz, 2012).

Most water treatment plants in the United States do not treat fluoride in water, but add fluoride into water for people's health benefits. Treatment plants usually contain coagulation, flocculation, sedimentation, filtration and disinfection steps to treat drinking water (CDC, 2015). However, there are some fluoride treatment plants in the United States, such as the Andrews Fluoride and Arsenic Treatment Plant in Andrews, Texas. This plant is the largest fluoride treatment plant in the United States and can remove high levels of arsenic and fluoride to a concentration of 2 ppm. The plant uses a fixed bed adsorption process with activated alumina

and can treat 5,000 gallons of water per minute (WaterWorld, 2014). High lime water softening processes found in treatment plants can also remove fluoride in water (Crittenden et al., 2012), though not anion exchange water softening systems.

Figure 2.1 shows the areas in the world that are affected by excessive fluoride in their groundwater. Figure 2.2 shows states in India, Figure 2.3 shows areas in Tanzania, and Figure 2.4 shows regions in South Africa that have excessive fluoride in their groundwater. Table 2.2 shows other countries in the world that are affected with high concentrations of fluoride in water, their locations, and the health effects of excessive fluoride.

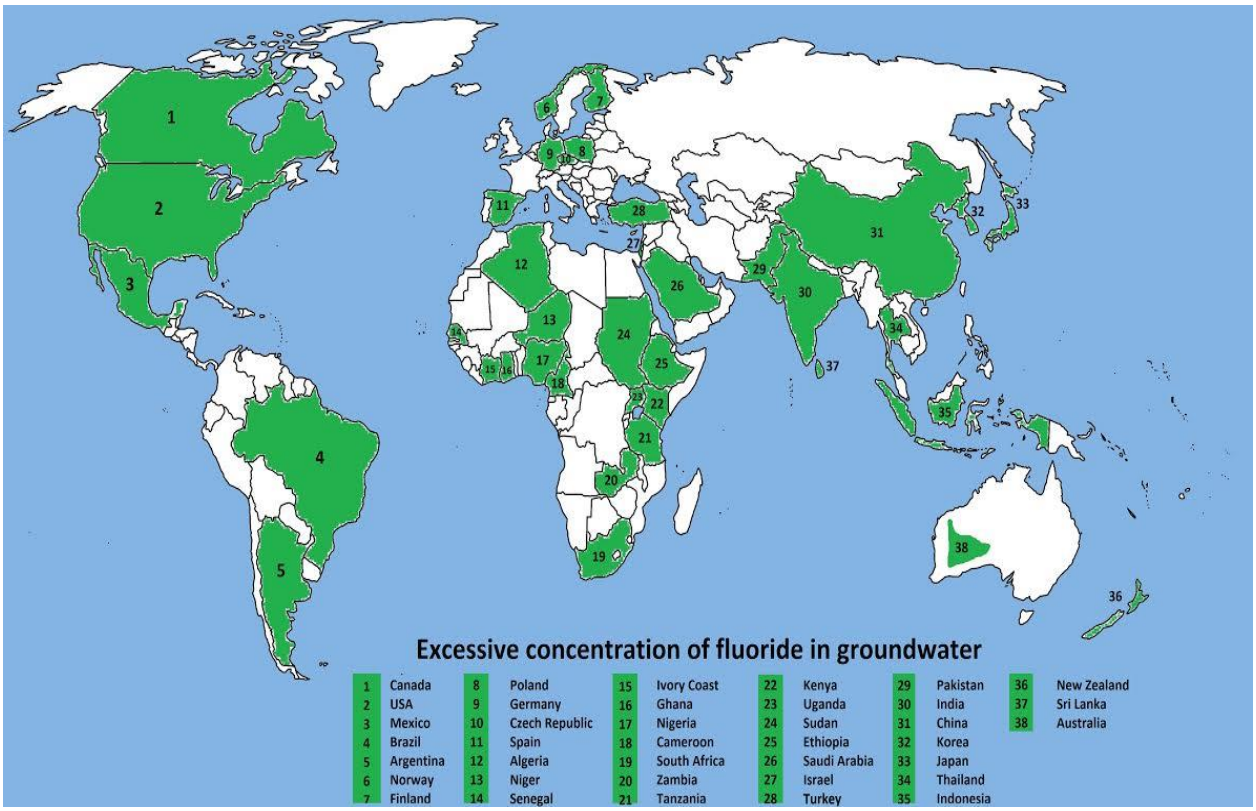

Fig. 2.1. Areas in the world that have excessive fluoride in groundwater. (Modified from WHO, 2004a)

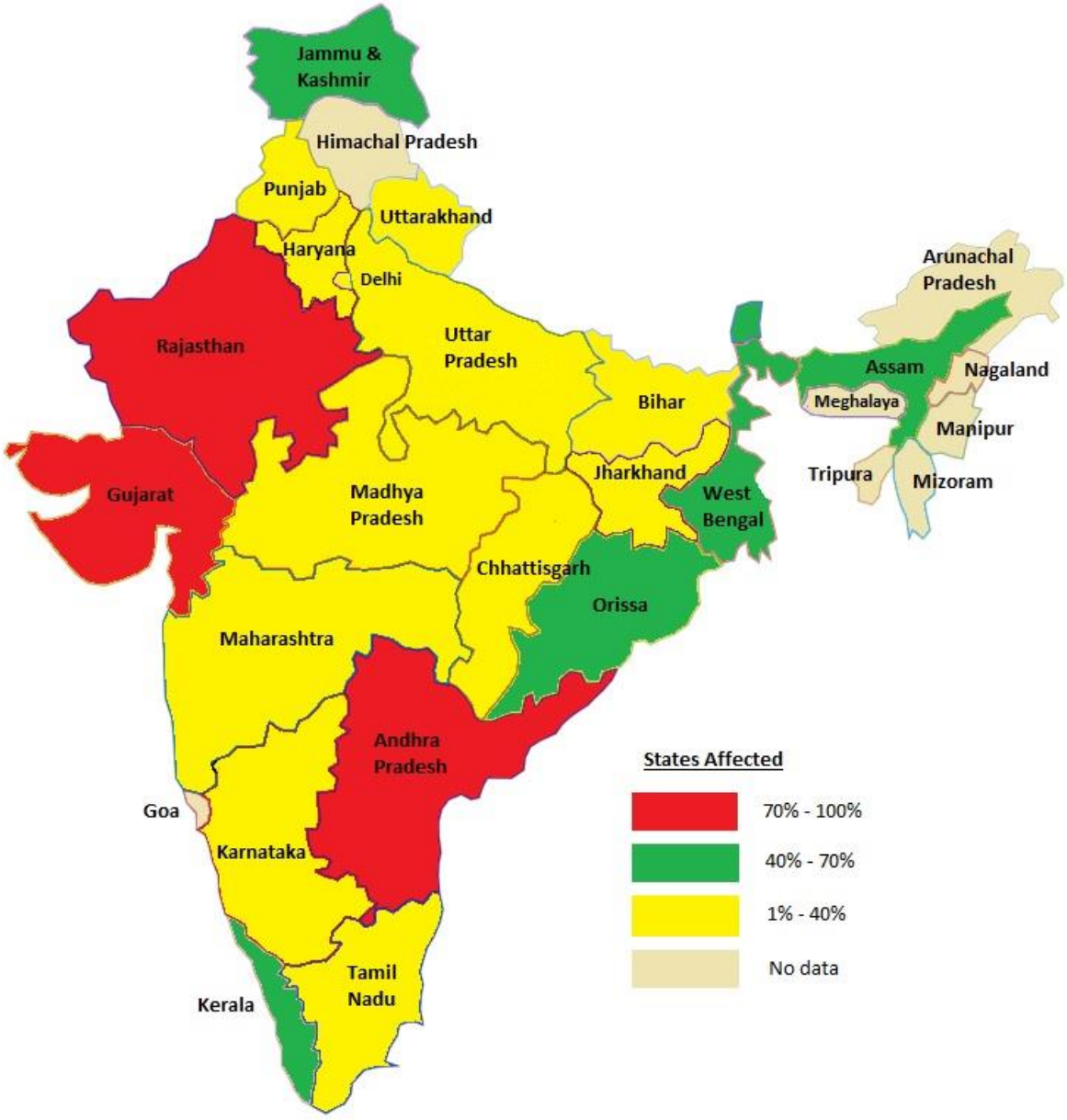

Fig. 2.2. States in India affected with excessive fluoride in water. (Modified from UNICEF, 1999)

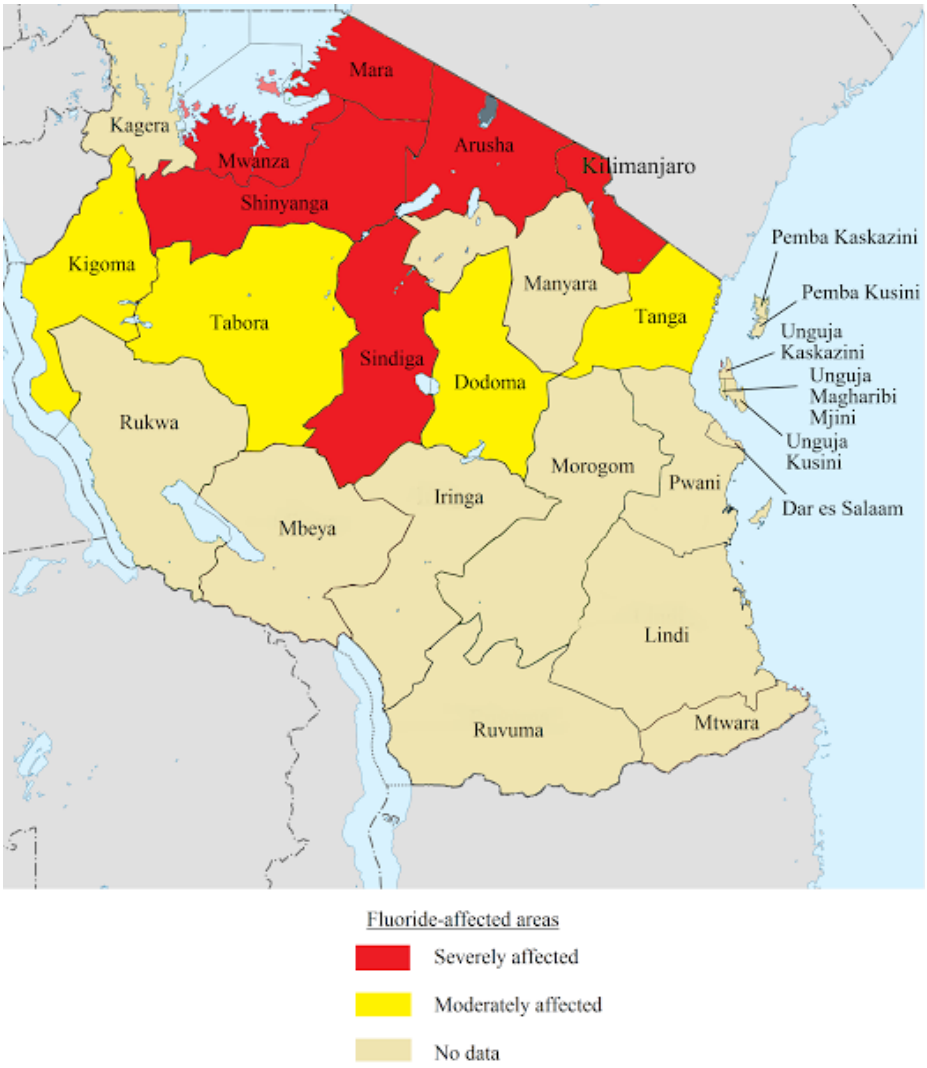

Fig. 2.3. Fluoride affected areas in Tanzania. (Modified from Mjengera and Mkongo, 2003)

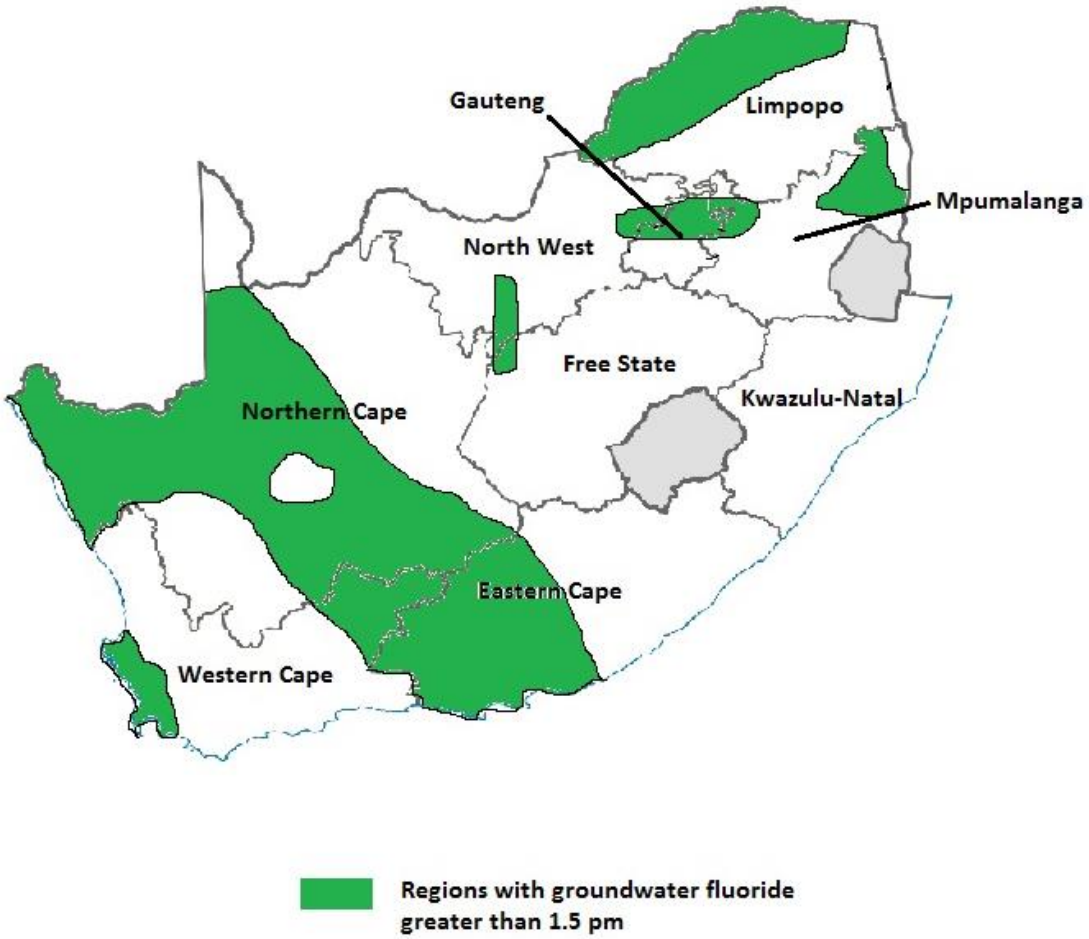

Fig 2.4. Regions in South Africa that have greater than 1.5 mg/L F^- in their groundwater. (Modified from McCaffrey and Willis, 2001)

Table 2.2. Countries in the world that are affected with high concentrations of fluoride in water, their locations, and the health effects of excessive fluoride.

Affected Countries	Description of Fluoride Levels and Health Affects	References
Mexico	Approximately 5 million people are affected by excessive fluoride in groundwater. In Abasolo, Guanajuato, 8 mg/L F- was found. In Hermosillo, Sonara, 7.8 mg/L F- was found. In rural areas, 0.9-4.5 mg/L F- has been found, while in urban areas 1.5-2.8 mg/L F- has been found	Diaz- Barriga et al.,1997
Ethiopia	In the Ethiopian Rift Valley, 1.5-177 mg/L F- has been found, especially in the Wonji-Shoa sugar estates. In the Main Ethiopian Rift Valley 80% of the whole population (80 million people) have exposure to high concentrations of fluoride. Approximately 1.2 million people drink from contaminated groundwater.	Haimanot et al.1987, ; Kloos et al.,1993 ; Rango et al., 2010
Canada	In Canada, Alberta has reportedly 4.3 mg/L F-, Saskatchewan has 2.8 mg/L F-, and Quebec has 2.5 mg/L F-. Rigolet and Labrador have a range of 0.1-3.8 mg/L F-, with Rigolet having reported cases of people with dental fluorosis.	Health Canada,1993 ; Ismail and Messer,1996 ; WHO, 2002
Poland, Finland, Czech Republic, Brazil, Indonesia, Israel, Turkey, Cameroon, Zambia, Europe	Czech Republic, Finland and Poland have fluoride concentrations higher than 3 mg/L. Brazil has 0.1-2.3 mg/L of fluoride in the northeast region of Paraiba and 2-3 mg/L in Ceara. Indonesia has 0.1-4.2 mg/L of fluoride in the wells of the " north-eastern part of Java in the Asembahus coastal plain." In the Negev desert regions of Israel, they have "natural waters" containing fluoride at 3 mg/L. Middle and Eastern Turkey has high concentrations of fluoride. For example, the Denizli- Saraykoy and Caldiran plains have reported 13.7 mg/L F-. There has also been reported incidents of dental and skeletal fluorosis in " Cameroon, Zambia and Europe."	Azbar and Turkman,2000 ; Cortes et al., 1996; Czarnowski et al.,1996; Heikens et al.,2005; Milgalter et al.,1984; WHO,2002, 2006; Oruc, 2008; Fantong et al.,2009; Fordyce et al., 2007; Shitumbanuma et al., 2007
Iovry Coast, Senegal, North Algeria, Uganda, Argentina	In the Guinguineo and Darous Rahmane Fall regions of Senegal, 30-60% of the children have severe dental fluorosis. They are exposed to 4.6-7.4 mg/L F-. In the "south-est subhumid pumpa regions" of Argentina, 0.9- 18.2 mg/L of fluoride have been reported. In Western Uganda in the Rift Valley area, 0.5-2.5 mg/L of fluoride has been found and people have had dental fluorosis. Algeria and Ivory Coast have also had people with incidences of fluorosis.	Brouwer et al., 1988; Paoloni et al., 2003; Rwenyonyi et al., 2000; WHO, 2005
Norway , New Zealand, Germany, Spain, Niger, Nigeria, Pakistan, Iran	Hordaland, Norway had groundwater with excessive fluoride at ranges of 0.02- 9.48 mg/L. In the Muenster regions of Germany, 8.8 mg/L F- was found, and in the Tenerife areas of Spain, 2.5 to 4.59 mg/L of F- have been found. In Tibiri, Niger, boys had skeletal flourosis when they were exposed to fluoride concentrations of 2.02-3.73 mg/L. In Langtang, Nigeria, 26.1% of the people exposed to 0.5-3.96 mg/L F- got dental fluorosis. In Naranji, Pakistan, 8-13.52 mg/L F- were found in springs and streams. Iran also has high fluoride levels of 8.85 mg/L in their drinking water and frequent occurences of dental fluorosis.	WHO,2005; Barsen et al.,1999; Hardisson et al.,2001; Queste et al., 2001; Shah and Danishwar, 2003; Wongdem et al., 2000; Poureslamie t al., 2008; Fekri and Kasmaei, 2011
Saudi Arabia, Eritrea, Sri Lanka, Thailand, Japan, Korea	In Mecca, Saudi Arabia, 2.5 mg/L of fluoride have been found, as well as 2.8 mg/L of fluoride in the Hail regions with people being affected by fluorosis. In Eritrea in the Keren areas, 2.02-3.73 mg/L have been found. In the Northern Central Province of Sri Lanka, up to 10 mg/L of fluoride have been reported, especially in areas that have less extensive rainfall and long-term leaching of fluoride from crystalline bedrock. In Thailand, 1% of the drinking water sources have fluoride in it at a concentration of 2-more than 10 mg/L. In Japan, of the people exposed to 1.4 mg/L F-, approximately 15.4% have been affected with dental fluorosis. In south east Korea, one fourth of the wells have greater than 5 mg/L of fluoride.	Akpata et al.,1997; Al-Khateeb et al.,1991; Dissanayake, 1996; Kim and Jeong, 2005; Srikanth et al., 2002; Tsutsui et al., 2000; Fawell et al., 2006

2.4 Current Defluoridation Treatment Systems

One can mitigate the effects of excessive fluoride in water by using alternative water sources, improving the nutrition in one's diet or removing fluoride from drinking water using defluoridation treatment systems. It has been shown through studies that calcium intake has a direct relationship to the reduced risk of dental fluorosis (Dinesh, 1998). Intake of vitamin C also helps reduce the risk of dental fluorosis (PCFI, 1993; Reddy and Deme, 2000; Krishnamachari, 1976). Improving one's nutrition can be a helpful supplement to preventing the negative impacts of excessive fluoride, but cannot be the ultimate solution. Therefore, people need other options, such as defluoridation treatment systems that are sustainable, affordable and easy to use by the local people.

There are several current defluoridation methods. Removal processes can be categorized into four main groups: "1) coagulation, 2) adsorption, 3) electrochemical methods, and 4) membrane processes." Coagulation processes involve using "chemical reagents such as lime, calcium, magnesium salts, poly aluminum chloride and alum" to form a precipitant with fluoride (Gupta and Ayoob, 2016). Adsorption involves using sorption media that is packed in columns. Fluoride containing water is cycled through the columns, and the media can be regenerated, renewed or disposed. Electrochemical methods can be categorized into two categories: electrosorptive and processes and electrocoagulation. Electrosorptive processes involve an "adsorbent bed" that is activated using an electric field. Electrocoagulation involves using "aluminum electrodes that release Al^{3+} ions that react with fluoride ions near the anode." Membrane techniques usually involve "reverse osmosis, nanofiltration, ultrafiltration, electrodialysis, and Donnan dialysis." (Gupta and Ayoob, 2016).

There are several defluoridation methods. However, a method that may be sustainable in one community may not be sustainable in other communities because of several factors, such as the stage of urbanization of a community. In industrialized communities, contact precipitation, activated alumina, synthetic resins, reverse osmosis and electrodialysis have been common fluoride removal methods. In developing communities, bone charcoal, contact precipitation, Nalgonda, activated alumina and clay have been common effective fluoride removal methods (Fawell et. al, 2006). In developing countries, the water treatment systems are mostly decentralized, which can be advantageous when the usage is more variable than centralized water systems. Decentralized systems can be changed to centralized systems (a "water works"), a village plant or household system. Also, there can be a continuous supply of defluoridated water using column filters or in batches using a water bucket. A benefit of decentralized systems is the ability to defluoridate water only used for drinking and washing, which would save resources and waste disposal (Fawell et. al, 2006).

Commonly used removal processes in developing countries can be categorized into four main groups: 1) sorption media using bone charcoal, activated alumina, clay and eggshells 2) precipitation chemicals using calcium and phosphate compounds, magnesium oxide and lime 3) co-precipitation chemicals using aluminum sulfate and lime 4) combination of adsorption and precipitation processes. Sorption media is preferably used in columns for a continuous supply and the media needs to be regenerated or renewed. For precipitation chemicals, fluoride reacts with the chemical reagents to form precipitants. Precipitation chemicals are sometimes added upstream of a catalytic filter bed. There is no sludge and no saturation of the bed, only buildup of precipitate in the bed. Co-precipitation chemicals need to be added daily to water and in batches, and results in sludge waste. Common compounds used are polyaluminum chloride and lime

(Fawell, 2006; Ayoob 2008). There are other mechanisms at work other than precipitation, such as “adsorption, occlusion or mechanical entrapment” (Ayoob, 2008; Ayoob and Gupta, 2016). When one treatment method is not sufficient, a combination of treatment methods can be used together or a treatment method can be enhanced, such as limestone adsorption columns enhanced with the addition of acids like acetic, oxic, citric and phosphoric acid. Both adsorption and precipitation is at work (Nath and Dutta, 2010; Gogoi et al., 2015; Nath and Dutta 2012).

2.4.1 Sorption Media

Adsorption is the adhesion of substances at a surface or interface. The mechanism can either be “physisorption”, “chemisorption” or both. Chemisorption is a stronger bond compared to physisorption. Ion exchange is a type of adsorption where “ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface” (Weber, 1972; Gupta, 2008). Ion exchange and adsorption are the most used defluoridation methods in recent years. Some adsorption materials for defluoridation include: activated alumina, apophyllite, bauxite, bentonite, brushite, calcite, acidic clay, kaolinite clay, china clay, charfine and nirmali seeds, chitosan, clinoptilolite, “diatomaceous earth”, “Fuller’s earth”, graphene, halloysite, hydroxyapatite, laterite, lignite, limestone powder, kaolinite, gibbsite, goethite, gypsum, magnesite, natrolite, “rare earth oxides”, pumice stone, quartz, serpentine, aiken soil, alkaline soil, “Ando soil”, stilbite, synthetic resins, vermiculite, and zeolite (Bower and Hatcher, 1967; Singano et al., 1997; Bhatnagar et al., 2011, Fawell et al., 2006, Fan et al., 2003; Turner et al., 2005; Murutu et al., 2012; Thole et al., 2012; Mourabet et al., 2011; Maiti et al., 2011; Asgari et al., 2012; Dutta et al, 2016). In a study by Srimurali et al., the fluoride removal capacity was found to be: bentonite > charfines > kaolinite> lignite> nirmali seeds. With adsorbents, higher

removal is achieved with decreasing particle size of the adsorbent and increasing dosage (Srimurali et al., 1998). The smaller the particle size, the more surface area will be available for adsorption.

These minerals all have metal lattice hydroxyl groups that can be exchanged with fluoride. An equation for a metal compound M (Fawell et al., 2006):

$$M\text{-}OH_{(s)} + F^- = M\text{-}F_{(s)} + OH^- \quad \text{Eq. (2.5)}$$

2.4.1.1 Bone Charcoal

Bone charcoal is a "blackish, porous, granular material," made up of 57-80% calcium phosphate, 6-10% calcium carbonate, and 7-10% activated carbon. It has an ability to adsorb fluoride because its chemical composition has two hydroxyl groups that can be exchanged with fluoride, $Ca_{10}(PO_4)_6(OH)_2$ (Fawell et al., 2006; Gupta & Ayoob, 2016). One of the most important aspects about bone charcoal is the preparation. Without proper preparation, the water may taste or smell like rotten meat, which would be unacceptable to the user. A good guideline is heating the bone charcoal for 4 hours at 550 $^{\circ}$C. The whole process of heating and cooling takes at least 24 hours and would depend on batch size and packing. The bone is heated in a pot in a potter's kiln without or with limited exposure to atmospheric oxygen. Another disadvantage is that bone charcoal is limited commercially now, but can still be made in the village or in the household.

Bone charcoal has low regeneration capacity. It is possible to regenerate the bone charcoal after it has been saturated with fluoride by adding 1 percent solution of sodium hydroxide and then washing the medium with caustic soda (AWWA, 1971). This, however, is

more suitable for large-scale water treatment systems. For small scale, village or household treatment systems, we can use the bone charcoal as fertilizer and soil conditioner (Fawel et al., 2006; Gupta & Ayoob, 2016).

The three most common defluoridation units shown below can be made relatively inexpensively, locally, durably using plastic, concrete or galvanized iron sheets. Figure 2.5 shows the three most common defluoridation units. However, the price of bone charcoal is more expensive. In 1995, the price for bone charcoal from UK, China and United Republic of Tanzania were $2280, $333 and $167/ton respectively. When made locally or in the household, bone charcoal can be more inexpensive, which was found in the Arusha region in the United Republic of Tanzania. 120 kg of charcoal was used per ton of bone (Fawell et al., 2006).

2.4.1.2 Activated Carbon and Clay

Other promising sorptive media include activated alumina and clay. Activated alumina is aluminum oxide (Al_2O_3) grains that have sorptive properties and a very high surface area, approximately 200-300 m^2/g (Gupta and Ayoob, 2016), which makes it a widely recognized adsorbent worldwide. Usually, they are put in a packed column. As water is allowed to flow through the column, pollutants adsorb to the surface of the grains until the column is completely saturated and the grains need to be regenerated. The capacity of alumina is dependent on the water's pH, with an optimum pH being 5.

Activated alumina on-site defluoridation systems, as well as hand pumps, have been implemented in India and by UNICEF. The treatment system consists of two chambers. The upper chamber is packed with 3-5 kg of activated alumina at a depth of 9-17 cm and has a micro filter and an orifice to keep the flow rate at approximately 12 L/h. There is a "perforated stainless

steel plate" on top of the AA bed to keep uniform distribution of water. Raw water is put into the upper chamber and percolates through the AA bed while the fluoride gets adsorbed by the alumina. Defluoridated water can be collected and drawn from the lower chamber (RGNDWN, 2001; Daw, 2004). The cost of activated alumina is estimated at US $0.975/ kg (COWI, 1998). A capacity of 6,750 – 11,760 g/m^3 has been reported from public water treatment plants. Additionally, regeneration of activated alumina is possible first with a caustic solution, which is usually 1% sodium hydroxide, followed by a dilute acid, usually 0.05 N sulfuric acid, and a water rinse (Gupta and Ayoob, 2016; Schoeman and MacLeod, 1987).

Clay is a sedimentary material that is made of fine particles of hydrous aluminum silicates and other minerals. Fired clay and powdered clay can be used to remove fluoride from water, as well as decrease turbidity. There have been many studies on soils around the world, such as Illinois soils, Ando soils, sodic soils, fired clay chips, fly ash, "clay pottery, activated clay, kaolinite, bentonite, illite, goethite", palygorskite, dolomite, smectite soils (Gupta and Ayoob, 2016). However, it has been found that removal efficiencies are low, around 67%, so clay shouldn't be used if water contains high concentration of fluoride or if there needs to be high removal efficiency. Researchers have tried to improved adsorption capacity by coating the clays and soils with alumina and iron hydroxides, Al_2O_3, $FeCl_3$, and $CaCO_3$ which improved the adsorption capacity (Argawal et al., 2003; Fawell, 2006) Still, clay and soils have not been found to have high enough removal rates to be of practical use. Figure 2.6 shows an example of a filter that is a stratified column of clay chips, pebbles and coconut shells used in Sri Lanka (Fawell et al., 2006).

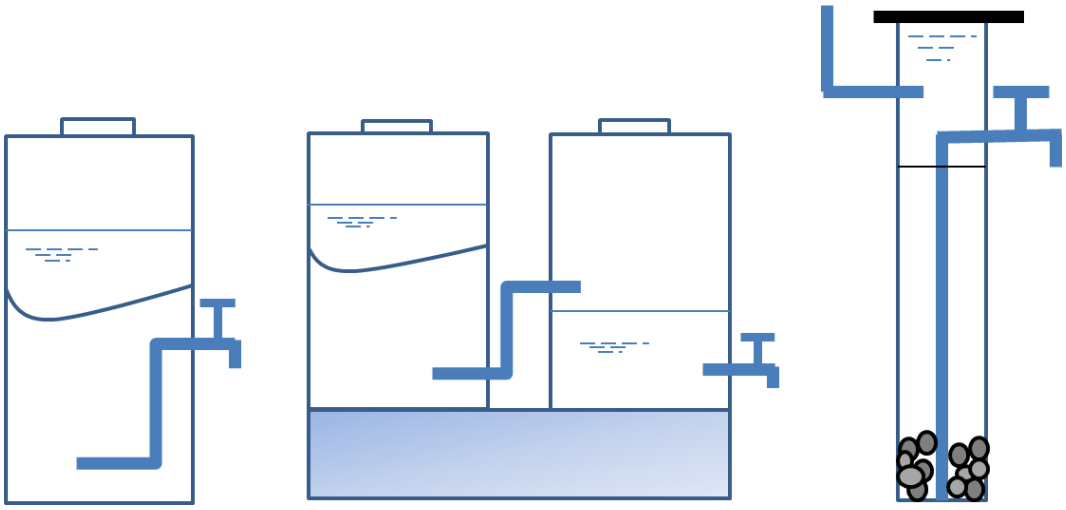

Fig. 2.5. Common defluoridation units (left to right: drum, double bucket, column filter) (Modified from Fawell et al., 2006)

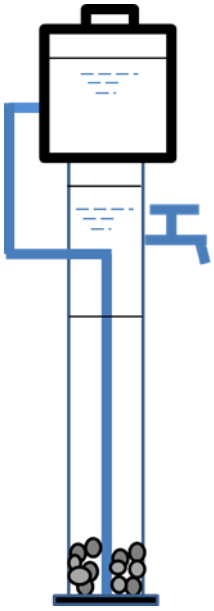

Fig. 2.6. Sri Lanka stratified column with clay chips, pebbles and coconut shells (Modified from Fawell et al., 2006).

2.4.1.3 Eggshells

Eggshells can also be a potential adsorbent used to defluoridate water, as shown in a study done by Bhaumik et al. (2011). Eggshells are composed of 94 % calcium carbonate, and approximately 6% calcite and calcareous soil (Abdel- Jabbbar and Al-ASheh, 2009). They are expected to be good biosorbents due to their porous and "cellulosic" structure, and because they contain amino acids (Kalyani et al., 2009). Furthermore, eggshells are inexpensive because they are waste products that are thrown into landfills (Clesceri and Greeberg, 1998).

For the experimental procedure, eggshells were collected from the local market in Bengal, India and were washed with distilled water and dried in a hot oven at 110 ^{o}F for 12 hours. The dried eggshells were grinded and sieved at different mesh sizes (200, 250, 300, 350 µm). The initial fluoride concentrations were tested at 7.1 mg/l and 10.0 mg/l. Adsorbent dose was 0.2- 2.4 g of eggshell/ 100 ml of water. A 100 ml of fluoride solution was shaken in a 250 mL Erlenmeyer flask with the eggshells for 1 hour at 250 rpm at 303 K in a batch experiment. The solids were then filtered out. The effluent fluoride concentration was measured through a spectrophotometer, and the adsorption capacity of the eggshell was determined by the equation: (Bhaumik, 2011).

$$qe = (C_i - C_f) * \text{Volume of Water/ Gram of Adsorbent} \quad \text{Eq. (2.6)}$$

To determine the adsorption characterics of the eggshell, Freundlich (Freundlich,1906), and Langmuir (Langmuir,1916) and Dubinin- Radushkevish (Oguz,2005) isotherm models were used.

$$\text{Freundlich equation: } q_e = K_f (C_f)^{1/n} \quad \text{Eq. (2.7)}$$

$$\text{Linearized Freundlich equation: } \log q_e = \log K_f + 1/n \log C_f \quad \text{Eq. (2.8)}$$

Langmuir equation: $q_e = (q_m\, b\, C_e)/(1 + b\, C_e)$ Eq. (2.9)

Dubinin- Radushkevish equation: $q_e = q_m \exp(-K\varepsilon^2)$ Eq. (2.10)

Es (mean free energy kJ/mol) = $1/\sqrt{2K}$ Eq. (2.11)

If Es is between 8 and 16 kJ/mol, the mechanism at work is an ion-exchange chemisorption mechanism. If Es is below kJ/mol, the mechanism at work is physical sorption.

Through the Langmuir isotherm, a q_m value of 1.09 mg/g was found. Eggshell's adsorption capacity was compared with other low cost adsorbents and it was found that eggshells have a higher adsorption capacity than activated carbon from *Dolichos lab* (0.233 mg/g), crude fibre content from neem, pipal and khair (0.04 mg/g), gibbsite (0.4 mg/g), kaolinite (0.2 mg/g), dolomite (0.21-0.29 mg/g), smectite (0.33 mg/g), brick powder (0.55 mg/g), used tea powder (0.054 mg/g) and calcium pretreated macrophyrte biomass (0.110 mg/g)(Fan et al, 2003; Kishorea and Hanumantharao, 2010; Jamode et al., 2004; Wijesundara, 2004; Nath and Dutta, 2010). Eggshells have a lower adsorption capacity than activated carbon from *Acacia Arabica* (2.06 mg/g) and Tamarind seed (6.09 mg/g) (Sujana et al., 2009; Jamode et al., 2004).

Experimental results showed that maximum adsorption occurred between pH of 2.0-6.0 and a maximum adsorption capacity of 1.09 mg/g. By using the Dubinin- Radishkevich isotherm model, it was found that the sorption mechanism from fluoride onto eggshell power was chemisorption because the "adsorption kinetics followed pseudo-second order kinetic model." The treatment system removed fluoride concentrations from 7.1 mg/l and 10 mg/l down to <1 mg/l with a dosage of 2.4 g of eggshell/ ml of water (Bhaumik, 2011). Using eggshell powder is a potential defluoridation adsorbent that is economical, inexpensive and easy to use. Potential further experiments should analyze how improve the adsorption capacity.

2.4.2 Precipitation Chemicals

2.4.2.1 Slaked Lime

$Ca(OH)_2$ reacts with fluoride to form insoluble calcium fluoride (CaF_2). To form calcium fluoride, other salts may be used such as $CaSO_4$ or CaF_2. Below is the precipitation reaction equation: (Gupta and Ayoob, 2016)

$$Ca(OH)_2 + 2F^- \rightarrow CaF_2 \downarrow +2\ OH^- \qquad \text{Eq. (2.12)}$$

There are many limitations to using just lime to precipitate fluoride: increase of pH, high residual concentrations (10-20 mg/L of fluoride), large volumes of sludge, poor settling of flocs, and hardness in water (Ayoob, 2008; Reardon and Wang, 2000; Wasay et al., 1996; Castel et al., 2000; Huang and Liu, 1999). Fluoride is only easily precipitated as CaF_2 at fluoride concentrations above 10-20 mg/L due to calcium fluoride's solubility product. At fluoride concentrations less than 10 mg/L CaF_2 is soluble and doesn't precipitate (Nath and Dutta 2010; McCann, 1968; Majima and Takatsuki, 1987). These limitations make lime precipitation with fluoride not a sustainable solution for deflouridation. There would need to be further enhancements and combinations of treatment methods.

2.4.2.2 Magnesium Oxide

Magnesium oxide can also react with fluoride to form insoluble magnesium fluoride. This has method has been used in onsite defluoridation systems where excessive fluoride is endemic. Below are the equations describing the reactions (Ayoob and Gupta, 2016; Lislie, 1967; Rao and Mamatha, 2004)

$$MgO + H_2O \rightarrow Mg(OH)_2 \quad \text{Eq. (2.13)}$$

$$Mg(OH)_2 + 2F^- \rightarrow MgF_2 \downarrow + 2OH^- \quad \text{Eq. (2.14)}$$

The con to this method is the increase of pH to 10-11. However, it can be easily solved by adding sodium bisulfate (0.15-0.20 g/L) to bring the pH down to 6.5-8.5. In case studies, onsite treatment systems using magnesium oxide had two twenty liter containers. Fluoridated water is mixed with magnesium oxide in the upper container using a "manually operated geared mechanical stirring device" for 5 minutes. The water is allowed to settle in the upper container for 16 hours so that the flocs can settle to the bottom of the container. Defluoridated water flows down to the lower container through an "elastic" pipe that is "fitted" with a fine filter to filter out the remaining small flocs or sludge. The lower container collects the defluoridated water which is mixed with sodium bisulfate to lower the pH (Ayoob et al., 2008; Ayoob and Gupta, 2016).

2.4.2.3 Calcium and Phosphate Compounds

Calcium and phosphate compounds such as calcium chloride ($CaCl_2 \cdot H_2O$) and monosodium phosphate ($NaH_2PO_4 \cdot H_2O$) can react with fluoride to create insoluble calcium fluoride or fluorapatite. Below are the equations that describe the reactions that are occurring (Ayoob et al., 2008; Gupta and Ayoob, 2016). Note that the solubility product for CaF_2 is 3.58 $*10^{-11}$, while the solubility product for fluorapatite is 8.6 $*10^{-61}$ at 34 ºC, which means that fluorapatite is essentially insoluble (McCann, 1968).

$$CaCl_2 \cdot 2H_2O = Ca^{2+} + 2Cl^- + 2\ H_2O \quad \text{Eq. (2.15)}$$

$$NaH_2PO_4 \cdot H_2O = PO_4^{3-} + Na^+ + 2\ H^+ + H_2O \quad \text{Eq. (2.16)}$$

$$Ca^{2+} + 2F^- = CaF_2 \quad \text{Eq. (2.17)}$$

$$5Ca^{2+} + 3PO_4^{3-} + F^- = Ca_5(PO_4)_3F \quad \text{Eq. (2.18)}$$

Precipitation occurs when calcium and phosphate compounds are mixed with water and go through a saturated bone charcoal medium in a column filter. The bone charcoal is used as a filter for the precipitate and as a contact bed to catalyze precipitation (Dahi et al., 1996). Without the contact bed, precipitation of calcium fluoride and fluorapatite would not be possible because of "slow reaction kinetics." Defluoridated water flows continuously from the bed to a clean water tank by gravity. A clean water tap is installed at the bottom of the clean water tank. Flow is controlled either by a "narrow tube arrangement" or by a valve to ensure proper contact time with the chemicals (Fawell et al., 2006; Dahi et al., 1996). If the contact time is too short, removal rates will decrease and chemicals may escape into the treated water. If the contact time is too long, calcium phosphate compounds may precipitate and removal rates will also decrease. Optimum contact times have not been determined, but 20 to 30 minute contact times have proven to be effective (Dahi, 1998). An effective dosage ratio is 2 to 1 calcium chloride to MSP. Though this is a simple process, the theoretical background is still not well or deeply understood.

Contact precipitation has many advantages. People will not need to continually observe the flow and effluent concentrations, fluoride removal rates are high, there is a low operating cost and there is no health risk. Many countries in Africa such as Tanzania and Kenya have performed this defluoridation process and have been able to treat fluoridated groundwater with fluoride concentrations up to 10 mg/L. The costs for calcium chloride and sodium dihydrogen phosphate was US $283 and US $780/ ton , respectively in 1996 (Fawell et al., 2006; Ayoob et al., 2008).

For a household unit, the raw water bucket starts empty and the control valve is completely closed. 1.5 litres of calcium chloride (CC) and sodium dihydrogenphosphate (MSP) are mixed with part of the raw water. Afterwards, as more of the raw water is added, complete mixing occurs. The flow control valve is then opened to allow slow flow not exceeding 0.5 m per hour (Figure 2.7).

For a community system, the process is similar to the household system. The control valve starts off completely closed. Part of the raw water is mixed with CC and MSP. As more of the raw water is added, complete mixing occurs. The valve is opened to allow for slow flow, not exceeding 0.5 m/hr or 0.5 cm/min (Dahi, 1998) (Figure 2.8).

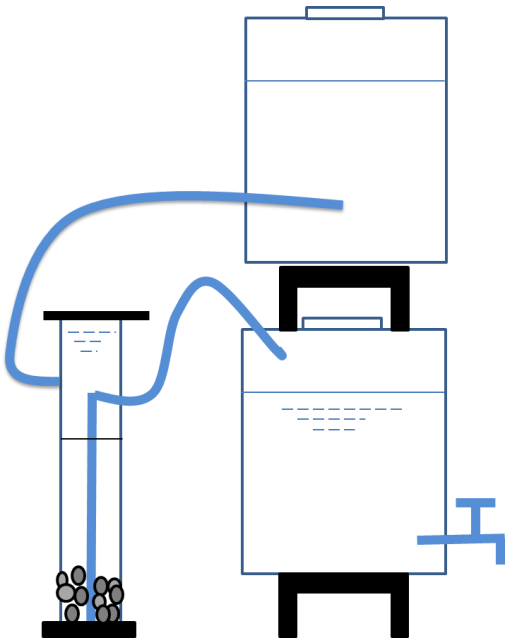

Fig. 2.7. Contact precipitation for a household system (Modified from Fawell et al., 2006)

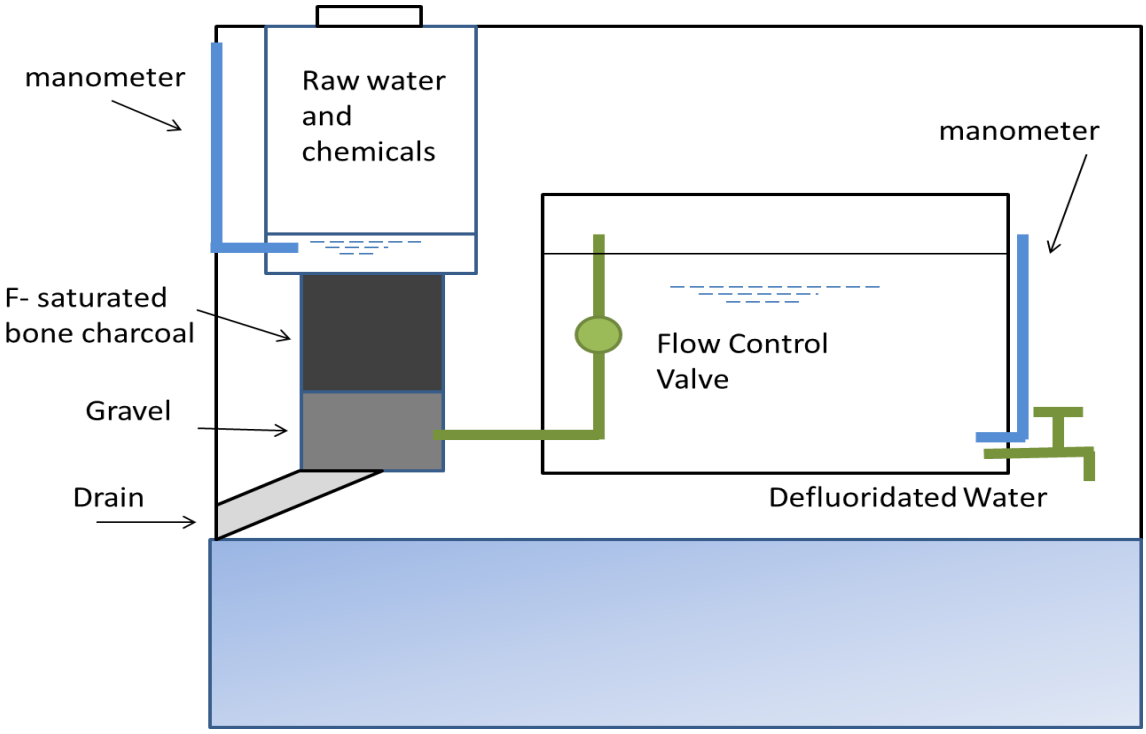

Fig. 2.8. Community system in Ngurdoto using contact precipitation (Modified from Dahi, 1998).

2.4.2.3.1 Case Study Analyzing Different Calcium Phosphate Systems

To find a more optimal calcium phosphate defluoridation system, several different combinations of calcium phosphate that form fluorapatite and hydroxyapatite have been analyzed (Pearce and Larsen, 1993; Bi et al., 1993; Wang et al., 1993). Materials studied were (He and Cao, 1996):

BSH: Brushite $CaHPO_4$
MCP: Monocalcium phosphate $Ca(H_2PO_4)_2$
TCP: Tricalcium phosphate $Ca_3(PO_4)_2$
HAP-I: Hydroxyapatite (He and Cao, 1996) method
HAP-II (Li and Lu, 1990) method
CCL: Calcium chloride ($CaCl_2$)
CH: Calcium hydroxide $Ca(OH)_2$
CCB: Calcium Carbonate $CaCO_3$
BC: Bone char, 80 mesh
PDP: Potassium dihydrogen phosphate KH_2PO_4
CL: Calcium lactate $(CH_3CHOHCOO)_2Ca$
FAP: Fluorhydroxyapatite

To make hydroxyapatite, 20 grams of calcium hydroxide were "allowed to react" with dilute phosphoric acid (200 ml with 1 part 85% H_3PO_4 and 5 parts water) for 4-6 hours followed by filtering through filter paper. pH was adjusted to 12 by continuously stirring NaOH into the solution. White precipitate was formed followed by 20-40 minutes of boiling, stirring, and filtering. The white powder obtained is hydroxyapatite (He and Cao, 1996).

Another way to make hydroxyapapatite is by taking $Ca(OH)_2$ paste and moderately mixing it into water at 60-90 ^oC until a saturated $Ca(OH)_2$ is formed. Phosphoric acid (1:5) is

then added with strong decrease the pH to 10-12. The white precipitant formed is hydroxyapatite (Li and Lu, 1990).

For the experimental procedure, 100 ml of fluoridated water was mixed for 1-2 min with different calcium phosphates followed by settling for 24 hours. pH was adjusted if necessary by using 0.1 N NaOH or HCl. Table 2.3 shows a summary of the experiment's findings. It shows that the lower the pH of the raw water, the better the removal rate for fluoride. For the tricalcium phosphate system, the more acidic the water, the greater the removal rate. The experiment also showed that if we only use one material, tricalcium phosphate (87%) would have the best removal rate followed by hydroxyapatite (68 %), followed by bone char (66.4%). Furthermore, adding more calcium materials to water containing calcium does not significantly improve the effectiveness of treatment system, shown by the bone char plus calcium chloride and bone char plus calcium systems. These systems showed no improvement from the bone char alone system. Additionally, adding phosphate materials to water containing calcium improves removal rates significantly, shown by the HAP II plus PDP system and the bone char and MCP system (Gongli and Yan, 1996). Both systems showed that when you add phosphate, removal rates increase from 60-70% to 95%. The best combination by comparing the different calcium phosphate systems seems to be the bone char and monocalcium phosphate. With 300 mg of bone char and 23 mg of monocalcium phosphate, one could remove fluoride from 10.4 mg/l to 0.6 mg/l after 24 hours of settling in a pH range of 6.5-8.5. (He and Cao, 1996).

Table 2.3. Removal rates of different calcium phosphate systems and different pHs (He and Cao, 1996)

Material	Removal of Fluoride (mg/l)	Comments
Bone Char (300 mg of BC / 100 mL of fluoridated water)	10.4 -3.6	
Bone Char & Calcium Chloride Bone Char & Calcium Lactate	10.4-3.6	no improvement from Bone Char alone
Bone Char & Brushite	10.4- (1.36-1.82)	~ 20% better than Bone Char alone
Bone Char & Monocalcium Phosphate	10.4 - (0.52-0.57)	~ 30% better than Bone Char alone. High Residual Phosphate= 10 mg/L
Monocalcium Phosphate & Calcium hydroxide & Calcium Chloride	10.32-0.71 (pHo = 5.05) 9.96-3.63 (pHo=9.01)	Has high efficiency for more acidic water
Tricalcium Phosphate	10.31-1.34 (pHo=7.62)	Can treat fluoride alone, lower the pH of water, better the removal rates
HAP I	10.52-1	
HAP II	12.04-3.80	
HAP II with KH_2PO_4	12.04- 0.21	Performed much better with the addition of more phosphate

2.4.3 Co-Precipitation Chemicals

2.4.3.1 Alum

Alum ($Al_2(SO_4)_3 \cdot 18H_2O$) is a widely used coagulant for flocculation & precipitation of contaminants in water. When alum is dissolved in water, the Al^{3+} ion goes through hydrolysis and forms $Al(OH)_4^-$. $Al(OH)_4^-$ reacts with F^- to form $Al(OH)_3F$ and OH^- . It is possible that part of the fluoride removal also occurs when F^- is precipitated with $Al(OH)_3$ flocs. The possible mechanisms that are occurring are precipitation of fluoride with hydroxide ions and aluminum ions, adsorption and "ligand exchange" (Qureshi and Malmberg, 1985, Peavy et al., 1985; Weber, 1972; Mekonen et al., 2001; Gupta et al., 2008). Efficiency of removal depends on pH, alkalinity of water, presence of coexisting anions, etc (Ayoob et al., 2008, Hao and Huang, 1986).

There are several cons to using alum only for defluoridation such as the high dosage of alum needed, sludge removal, high pH of defluoridated water, and the residual alumina remaining (Gupta et al., 2008, Choi and Chen, 1979). The presence of sulfate and aluminum ions into the defluoridated water is also a concern (Bulusu,1984; Gupta et al., 1999). Furthermore, with higher pH comes the increase of alum residuals. At pH of 9.8, 0.37 mg/L of alum residuals remain; At pH of 7.61, 0.07 mg/L of alum residuals remain. It has been found that a good range for pH in the alumn coprecipitation process is 5.5-6.5 (Sujana et al., 1998; Qureshi and Malmberg, 1985).

2.4.3.2 Alum and Lime (Nalgonda Method)

The co-precipitation process or the Nalgonda process was founded in India by the National Environmental Engineering Research Institute (NEERI) for household or community water treatment systems. The process was named after the first place that this treatment system was implemented. Aluminum sulfate, $Al_2(SO_4)_3{\cdot}18H_2O$, is added (700-1,200 mg/l) and dissolved in water using stirring and ensuring complete mixing. Alumnium hydroxide flocs are formed and settle to the bottom of the unit. Fluoride is "partially removed by electrostatic attachment to the flocs". Lime is then added to neutralize the pH, as adding alum results in acidic water. Additional lime is added to help with settling of the flocs. The dosage of lime is 4-5% of the amount of aluminum sulfate used (Bulusu et al., 1993; Ayoob and Gupta, 2016). Below are the equations that describe the chemical processes that are occurring (Fawell, 2006).

$$Al_2(SO_4)_3{\cdot}18H_2O = 2Al^{3+} + 3SO_4^{2-} + 18H_2O \quad \text{Eq. (2.19)}$$

$$2Al^{3+} + 6\,H_2O = 2Al(OH)_3 + 6H^+ \quad \text{Eq. (2.20)}$$

$$F^- + Al(OH)_3 = \text{Al-F complex} + \text{undefined product} \quad \text{Eq. (2.21)}$$

$$6\,Ca(OH)_2 + 12\,H^+ = 6Ca^{2+} + 12H_2O \text{ (for pH adjustment)} \quad \text{Eq. (2.22)}$$

One bag of aluminum and lime defluoridates one bucket of water. The villagers are taught to mix fast with a wooden spoon for one minute and then slowly for three minutes. The flocs settle for an hour and then the treated water runs from the first bucket to the cloth filter into the treated water bucket. The aluminum hydroxide flocs are loosely bound to the fluoride so treated water must be separated from the flocs in less than a few hours and precipitate should be discarded after flocculation process (Dahi et al. 1997). The price of one of the treatment buckets

in the United Republic of Tanzania was about TZS 3,000, which is US $3.3 in 1995 (COWI, 1998). Seven aluminum sulfate and lime bags cost US$0.15. (COWI, 1998). In addition to defluoridation, disinfection also helps to ensure safety of the water. Bleaching powder was added to the fluoridated water at 3 mg/L for disinfection purposes (Ayoob and Gupta, 2016) (Figure 2.9).

Treatment efficiency of the Nalgonda method is around 70 percent, so it may not be suitable for raw water with high fluoride contamination. Other limitations include high aluminum sulfate dosage, difficulty to know the amount of alum and lime to add, residual sulfate making the water salty, hardness of the water, high resulting pH of the treated water, and high amount of aluminum residuals (Ayoob et al., 2008; Mjengera and Mkongo, 2003; Fawel et al, 2006; Susheela, 2003). Below are other figurations of the Nalgonda process for household and community use (Figure 2.9 and Figure 2.10).

2.4.4 Combination of Adsorption and Precipitation Chemicals

2.4.4.1 Crushed Limestone with the Enhancement of Citric, Acetic and Oxalic acid

Precipitation of fluoride as CaF_2 using calcium containing salts is not effective at fluoride concentrations below 10-20 mg/L due to the solubility of CaF_2. Therefore, an alternative is to use different acids to bring the pH of the fluoridated water down so that dissolution of calcium salts can occur. With the increase of Ca^{2+} ions in the water, more CaF_2 precipitants can form. The water is neutralized by the addition of calcium salts which makes the water within drinkable limits (Dutta and Nath, 2010). Different acids have been tested such as acetic acid and citric acid. Acetic and citric acid were chosen because they weren't harmful to the body and didn't affect taste of the water. The acids are also cheap: $1.56 for 1 kg of acetic acid and $1.95

for 1 kg of citric acid. The treatment method for the acids would only cost $0.01 per liter of water treated. Limestone was used because it is a very accessible material in central Assam, India and inexpensive. Limestone had a chemical composition of 85-90% $CaCO_{3.}$ (Nath and Dutta, 2010; Dutta et al., 2006; Taher and Ahmed, 2001; Heaman et al., 2002).

For the experimental procedure, 0.05 M of Acetic acid and 0.033 M of Citric Acid were added into fluoridated water before being mixed in with crushed limestone in two different batch experiments. The crushed limestone had a diameter of 3-4 mm. The concentration of fluoride went down from 10 to 1.5 mg/L using 0.05 M of acetic acid and 0.033 M of citric

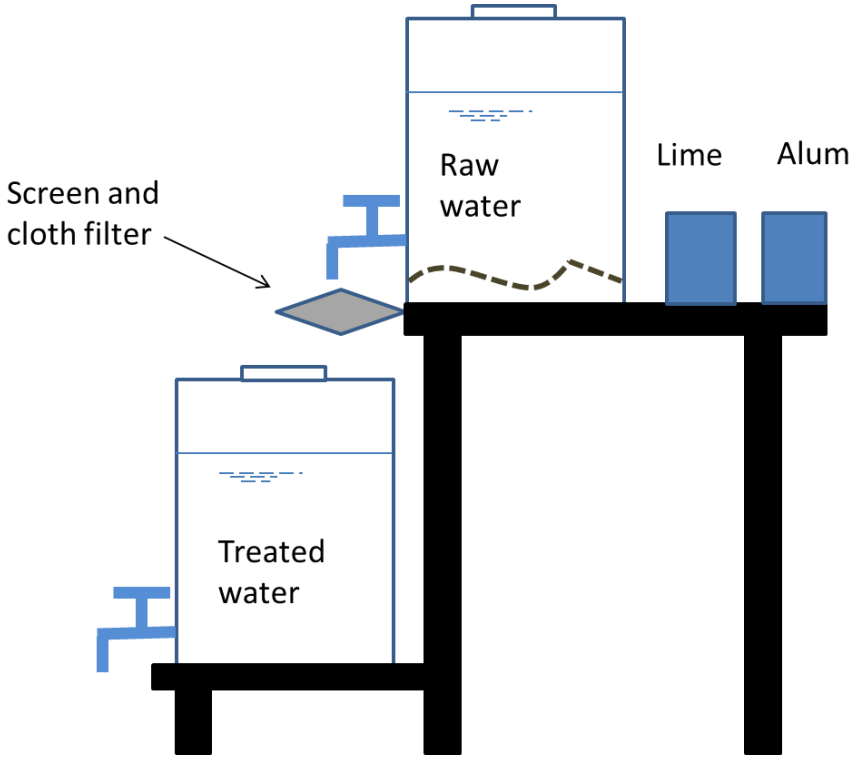

Fig. 2.9. Nalgonda defluoridation unit for household use in the United Republic of Tanzania (Modified from Dahi et. al, 1996)

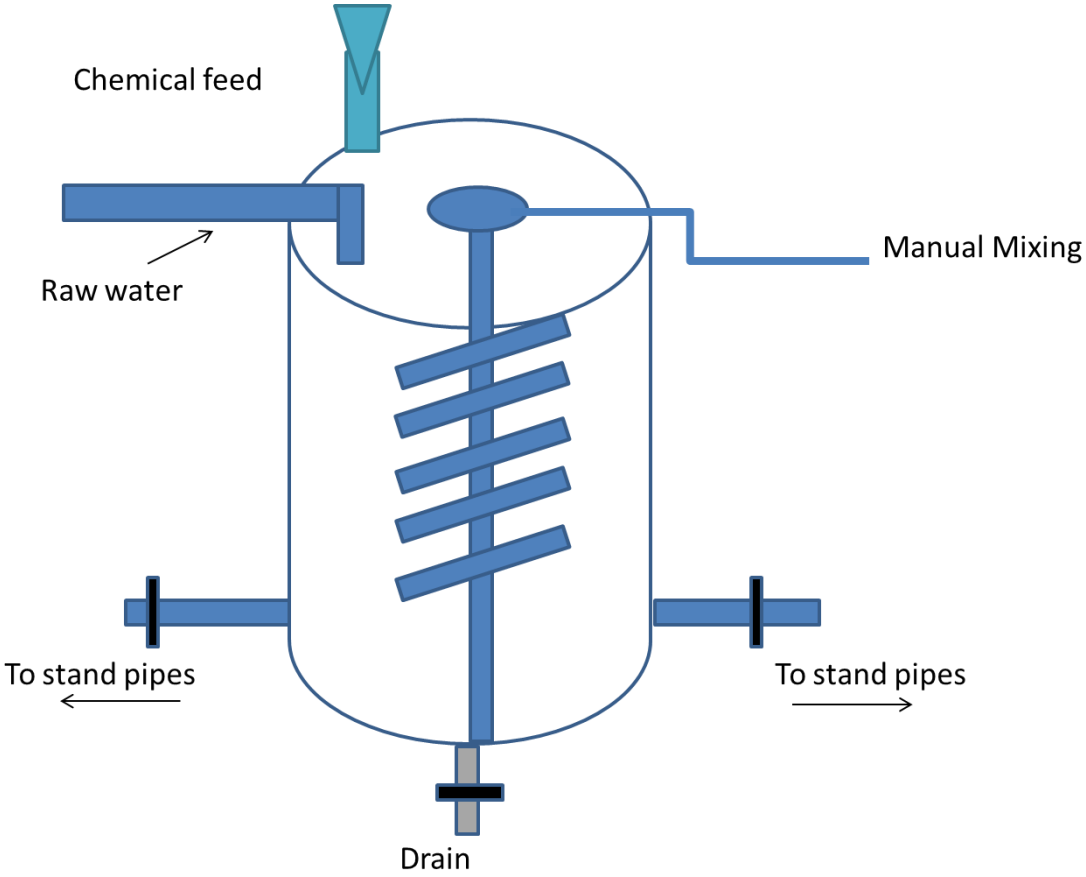

Fig. 2.10. Nalgonda defluoridation treatment for domestic and community use (Modified from Bulusu et al., 1993).

acid. The contact time was 12 hours and the final pH was approximately 6.2 to 7.0 for the citric acid experiment and 5.7 to 7.0 for the acetic acid experiment.

Another acid to use with the crushed limestone is oxalic acid. Dutta and Nath compared the results of oxalic acid with citric acid and acetic acid. Fluoridated water was pre-acidified with oxalic acid. Varying amounts of initial fluoride concentrations (5, 10, 15, 20 mg/L) were tested with varying amounts of oxalic concentrations (0.01, 0.05, 0.1 M).) 0.01, 0.05 and 0.1 M of oxalic acid made the fluoridated water to a pH of 2.17, 1.61, and 1.4 respectively (Nath and Dutta, 2012). The initial pH of the water was 6.80. (Das et al., 2007). Fluoride removal effectiveness increased with oxalic concentrations. There was 95% removal of 10 mg/L of fluoridated water by using 0.1 M of oxalic acid. Effectiveness was only gradually improved with increasing contact time from 6-24 hours. Therefore, a contact time of 6-12 hours would be appropriate, resembling a person leaving the treatment system to sit overnight. The amount of limestone chips needed was 1 kg of limestone chips per liter of water treated and the cost for the treatment method was estimated to be $0.1398 when using 0.1 M of oxalic acid. Oxalic acid costs approximately US$ 11.03 / kg and limestone costs approximately US$ 0.007 /kg. 12.6 grams of OA was used and 0.085 kg of limestone was used (Nath and Dutta, 2012).

Removal was observed to be caused my two mechanisms: precipitation of calcium fluoride and adsorption of F^- onto the crushed limestone surfaces. The oxalic acid increased H^+ ion concentration, dissolving the limestone and increased dissolution of the $CaCO_3$, causing an increase of Ca^{2+} ions (Yang et al., 1999; Reardon and Wang, 2000). Below are the equations describing the effect of pH on Ca^{2+} ion concentration.

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \downarrow \quad \text{Eq. (2.23)}$$

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \downarrow \quad \text{Eq. (2.24)}$$

The Ca^{2+} ions then precipitated with fluoride and oxalic acid forming calcium fluoride and calcium oxalate (Nath and Dutta, 2012). Treatment effectiveness only decreased slightly with the presence of other anions (NO_3^-, Cl^-, Br^-, SO_4^-, PO_4^{3-}), but not enough to a make significant difference. Amount of negative impact of the anions was found to be in the order of "phosphate> sulfate>bromide>chloride> nitrate" (Nath and Dutta, 2012; Shen et al., 2003; Sujana et al., 1998). The final pH of the water was found to be 6.5-7.5. Below is the chemical equation describing the mechanism that is occurring: (Nath and Dutta, 2012; Nath and Dutta, 2010)

$$CaCO_3 + C_2O_4H_2 \rightarrow Ca^{2+} + C_2O_4^{2-} + H_2O + CO_2 \uparrow \quad \text{Eq. (2.25)}$$

For the experimental procedure, limestone was crushed to a diameter of 2-3 mm in a column that was 44 cm in length and 4 cm in diameter. The total volume of water was approximately 200 mL. The columns were filled once a day and discharged partially at 6, 12 and 24 hours. The next day, the column would be filled with new fluoridated water. This was to mimic the water flow in an actual treatment system, which would not be a continuous flow system (Natha and Dutta, 2012).

Oxalic acid was found to be more effective than acetic acid and citric acid. Oxalic acid is a stronger acid than AA and CA, which means that there would be more dissolution of $CaCO_3$ and more Ca^{2+}. Furthermore, calcium oxalate has a lower solubility product constant and is less soluble, which means little residual oxalate would be left in the water and would be precipitated (Nath and Dutta, 2012). Neutralization of the oxalic acid solution by limestone occurred within minutes, which was much faster than that of AA and CA.

It is also important to note which processes are occurring at which stage of the defluoridation treatment. Saturation Index of CaF_2 can tell us whether adsorption or precipitation is the main mechanism at work at each stage of the treatment process. One can measure the

concentrations of the fluoride and calcium ions and compare them to the solubility product of CaF_2. The positive number would indicate "supersaturation" and "precipitation of CaF_2." A negative number would indicate that the main mechanism at work is adsorption. Below is the equation for calculation saturation index: (Nath and Dutta, 2010; Turner et al., 2005)

$$SI = \log_{10}\{\frac{(activity\ of\ Ca^{2+})(activity\ of\ F^{-})^2}{solubility\ product\ of\ CaF_2}\} \quad \text{Eq. (2.26)}$$

At the first and second water cycle, the SI index was negative and increased to a positive number after the fourth water cycle. Adsorption is the dominant mechanism in the first few water cycles, and the reason why fluoride concentrations can be reduced to ~ 1 mg/L F^-. After the fourth cycle, precipitation is the dominant mechanism because the adsorption sites on the limestones being saturated through continual use of the limestone column (Nath and Dutta, 2012; Turner et al., 2005). Furthermore, since neutralization of the treated water happened within minutes, it can be inferred that precipitation of CaF_2 by oxalic acid and limestone is completed quickly. Note that a significant reason this treatment process was effective was that it involved both precipitation and adsorption. Just using precipitation of CaF_2 would only remove fluoride concentrations down to around 10 mg/L because of the solubility product constant. However, adsorption is not restricted by the solubility product and can remove fluoride even at low concentrations (Nath and Dutta, 2012).

A concern about this treatment method is the calcium oxalate in the treated water. Kidney stones are 80% made of calcium oxalate and formation of them depends on the oxalate intake of a human. Calcium oxalate also forms during metabolism and deposits in the kidney. However, this shouldn't be of big concern because commonly eaten seeds and leaves have 10-100 times higher concentration of oxalate than that in treated water. Also, our bodies only absorb

2-5% of our oxalate intake (Holmes and Kennedy, 2000; Bhatt and Paul, 2008). Furthermore, since calcium oxalate is insoluble in waters with neutral pH, one could solve this problem by slightly increasing the pH of the water to about 8.0 by adding 0.1 g/L of $NaHCO_3$ and filtration (Noonan and Savage, 1999).

2.4.4.2 Crushed Limestone with Enhancement of Phosphoric Acid

Another defluoridation method that has been reported is the PA-crushed limestone treatment (PACLT) technique which uses limestone and phosphoric acid to treat excessive fluoride. This method has shown to have very effective results, treating fluoride concentrations from 0.526 mM to 0.5-52.6 µM with final neutral pH in treated waters (Gogoi et al., 2015). Various amounts of phosphoric acid (10,50, and 100 mM) was used, as well as 400 mL of fluoridated water and crushed limestone with a diameter of 2-3 mm in a plug flow fixed bed reactor with a capacity to hold a volume of 600 mL. The fluoride removal reached equilibrium at approximately 3 hours. Using 10mM of phosphoric acid increased the removal capacity of limestone from 0.39 mg/g to 1.01 mg/g and treated 106 L of water per kg of limestone (Biswas et al., 2009; Gogoi et al., 2015). The cost of this system was approximated to be \$0.58/ m^3 of water treated, which is a lot lower than other acids: \$12/m^3 of water treated for acetic acid, \$48.8/ m^3 for citric acid and \$139.8/ m^3 for oxalic acid. Regeneration of the limestone is possible by scrubbing, "soaking in 300 mM of calcium hydroxide" for 24 hours, and "soaking in NaOH for 24 hours followed by rinsing with water." All three methods regenerated removal efficiency by 50% (Gogoi et al., 2015).

The main reason this treatment method is so much more effective than using the other acids is because of the "sorption or exchange of fluoride by the calcium phosphates." All

the systems using limestone and acids have precipitation of CaF_2 and adsorption on limestone occurring. Below are the equations describing the mechanisms in the PACLT method: (Gogoi, 2015)

$$CaCO_3(s) + 2H_3PO_4 \rightarrow Ca^{2+} + 2H_2PO_4^- + CO_2^- + H_2O \quad \text{Eq. (2.27)}$$

$$CaCO_3(s) + 2H_2PO_4^- \rightarrow Ca^{2+} + 2HPO_4^{2-} + CO_2^- + H_2O \quad \text{Eq. (2.28)}$$

$$Ca^{2+} + F^- \rightarrow CaF_2(s) \downarrow \quad \text{Eq. (2.29)}$$

$$5Ca^{2+} + 3HPO_4^{2-} + 4OH^- \rightarrow Ca_5(PO_4)_3OH(s) \downarrow + 3H_2O \quad \text{Eq. (2.30)}$$

$$Ca_5(PO_4)_3OH(s) + F^- \rightarrow Ca_5(PO_4)_3F(s) + OH^- \quad \text{Eq. (2.31)}$$

The dissolution of $CaCO_3$ by phosphoric acid, "the precipitation of CaF_2 and the precipitation of calcium phosphate hydroxide are completed rapidly" (Gogoi et al., 2015) (Eq. 2.27, Eq. 2.29, Eq. 2.30). The sorption of fluoride with hydroxyapatite ($Ca_5(PO_4)_3OH$) is completed in about 3 hours (Eq. 2.31) and the neutralization of pH takes over 24 hours. The pH of the acidified water was 1.6 using 100 mM of PA (Gogoi et al., 2015). The pH rose significantly after just a few minutes, signifying the fast precipitation reaction between limestone and phosphoric acid and neutralization of "phosphoric acid by limestone." This fast reaction is probably due to the "high affinity" calcium phosphates have toward fluoride (Yu et al., 2011; Shan et al., 2009; Gogoi et al., 2016). Note that though neutralization of pH takes over 24 hours, most all the removal is finished by 3 hours, which shows us that significant removal is caused by physisorption of fluoride by hydroxyapatite.

This PACLT method was applied in a field trial in Assam, India for a small community and for 5 households. The community unit had a capacity to treat 220 L of water, while the household units had a capacity to treat 15 L of water at a time. They treatment units have treated water consistently up to 250 cycles. The PACLT treatment system could remove

fluoride concentrations down to 0.001 mg/L (Dutta et al., 2016). By using 0.68 mM of phosphoric acid and limestone rocks with diameters of 5-20 mm in a plug flow reactor, the PAELD system could decrease fluoride concentrations of 2.8- 20 mg/L to 0.58-0.81 mg/L. It was estimated that 1 kg of limestone could treat 149 L of water and the treatment method costed \$0.28 per m^3 of water treated (Dutta et al., 2016).

For the household unit, a 15 L container was used to first mix phosphoric acid with the raw water. 85% phosphoric acid was diluted ten times and it was calculated that 6.94 mL of 8.5 % phosphoric acid was needed for 15 L of water. The water would be transferred to the upper container with a capacity of 40 L which had 0.2-2 cm limestone chips and a "water holding" capacity of 15 L. After a residence time of 3 hours, water would be transferred to the lower container which had a capacity of 40 L and contained a four layered filter: sand, crushed limestone, sand and gravel filter. In the community unit, a 500 L plastic container was first used to mix the phosphoric acid and raw water. A 500 L plastic container was used as the limestone chip plug flow reactor with a water holding capacity of 280 L, and a 1,000 L plastic container was used to contain the four layer filter. Fluoride safe water would come out of the filter container (Dutta et al., 2016).

With 45% recovery of the limestone after scrubbing and rinsing regeneration, a total of 149 L of water can be defluoridated per kg of limestone, which gives a capacity of limestone in the PACLT method as 1.20 mg/g. This capacity was even better than the capacity found in laboratory tests. A reason why the pilot test had better removal results than laboratory tests is because the limestone chips were of smaller size: 1.0-1.5 cm in the laboratory tests compared to 5-20 mm used in the pilot tests. Having smaller particle sizes increases the surface area for adsorption to occur. This method had better removal capacity than other adsorbents,

such as limestone (0.39 mg/g) , activated alumina (1.08 mg/g), activated carbon (1.1 mg/g) and bone char (1.4 mg/g). It has lower capacity than hydroxyapatite nanoparticles (5.5 mg/g) (Biswas et al, 2009; Maliyekkal et al., 2006; Ramos et al., 1999; Dahi and Nielson, 1997; Poiner et al., 2011). The final pH of the water was 7.45- 7.90 and treatment was not affected by coexisting ions. The PACLT is a very cost-effective treatment method with high removal rates and small amount of resulting sludge. It is a very simple and maintainable treatment method for local users.

2.4.5 Treatment Systems That Treat Multiple Contaminants Simultaneously

Oftentimes, there are different contaminants in the water, so a treatment system that can treat different contaminants simultaneously is of great value. Arsenic is another widespread contaminant in drinking water that causes many detrimental health effects to people. In several places of the world, such as China, Latin America (especially in Mexico, Argentina and Chile), and the Main Ethiopian Rift, fluoride and arsenic occur concurrently in groundwater (Wen et al., 2003, Alarcon-Herrera et al., 2013, Rango et al., 2010). The waters that contained both fluoride and arsenic usually were in locations with mining activity, or geothermal, volcanic activity that had rocks containing, shale, and rhyolite (Lopez et al., 2012; Birkle and Merkel, 2000; Nicolli et al., 1989). Rhyolite is composed of quartz, orthoclase, sanidine, illite, and volcanic glass. Volcanic glass has been known to contain arsenic and fluoride (Alarcon-Herrera et al., 2013; Gutierrez et al., 2009; Onishi and Sandell, 1955; Robertson, 1989). Additionally, the waters that contain both arsenic and fluoride are usually alkaline and contain Na-HCO_3^- in a location that has semi-arid, arid climate. For arid, semi-arid regions, “chemical weathering” occurs more and there are higher evaporation rates. The solutes in the water are more concentrated and the water

becomes more saline, causing the pH of the water to rise and become alkaline. This causes arsenic and fluoride to desorb off of the rocks and into the water (Robertson and Megaw, 2009; Welch et al., 1988). The mining areas of Mexico, which has water contaminated with arsenic and fluoride, has high concentrations of Na^+ and HCO_3^-, as well as the waters in the Main Ethiopian Rift (Alarcon-Herrera et al., 2013; Rango et al., 2010). Figure 2.11 shows areas in China where there are high occurrences of arsenic and fluoride in groundwater.

Common methods that treat multiple contaminants concurrently, such as fluoride, arsenic and pathogens, include using coagulation, settling and filtering out of the contaminants through sand beds (Srimurali et al., 1998). "Reverse Osmosis, ion exchange, lime softening, adsorption on iron oxides or activated alumina" have also been analyzed (Kartinen and Martin, 1995; Domenec et al., 1996). Additionally, several low cost materials have already been studied, such as "kaolinite, bentonite, charfines, lignite and pumice," to see if they remove fluoride, arsenic and pathogens (Lounici, et al., 1997; Meng et al., 2001; Burhanettin et al., 2003). Devi et al. (2008) did an experiment using a homemade slow sand filter to treat fluoride, arsenic and bacteria.

For the experimental procedure, two tanks were used with a diameter of 30 cm and a height of 100 cm attached with an "outlet pipe, a drain valve and an outlet tap." One tank was filled with a layer of 10 cm of pebbles, a layer of 8 cm of filter gravel with sizes ranging from 0.8-1.5 mm, and a layer on top of 40 cm of deep filter sand with sizes ranging from 0.2-0.8 mm. The second tank also had the same layering except that there was a 10 cm crushed brick with grain size ranging from 0.25-0.5mm between the sand layer and gravel layer. The filtration rate was between 0.21 l/h and 1.2 l/h. The treatment system with the added crushed bricks had

effective removal rates from initial concentrations (5 mg/L for fluoride, 0.13 mg/L of arsenic and $2*10^9$ cells/100 ml of bacteria): 85.6 % of fluoride, 93.07 % of arsenic, 100% of coliform bacteria. The residual concentration of fluoride, arsenic and bacteria was 0.72 mg/l, 0.009 mg/l, and 0.009 mg/l respectively. Equilibrium time was at 10 hours. The treatment system without the crushed bricks had 60%, 54% and 100% removal of fluoride, arsenic and bacteria respectively. Table 2.4 shows a summary of the treatment methods explained in Chapter 2.

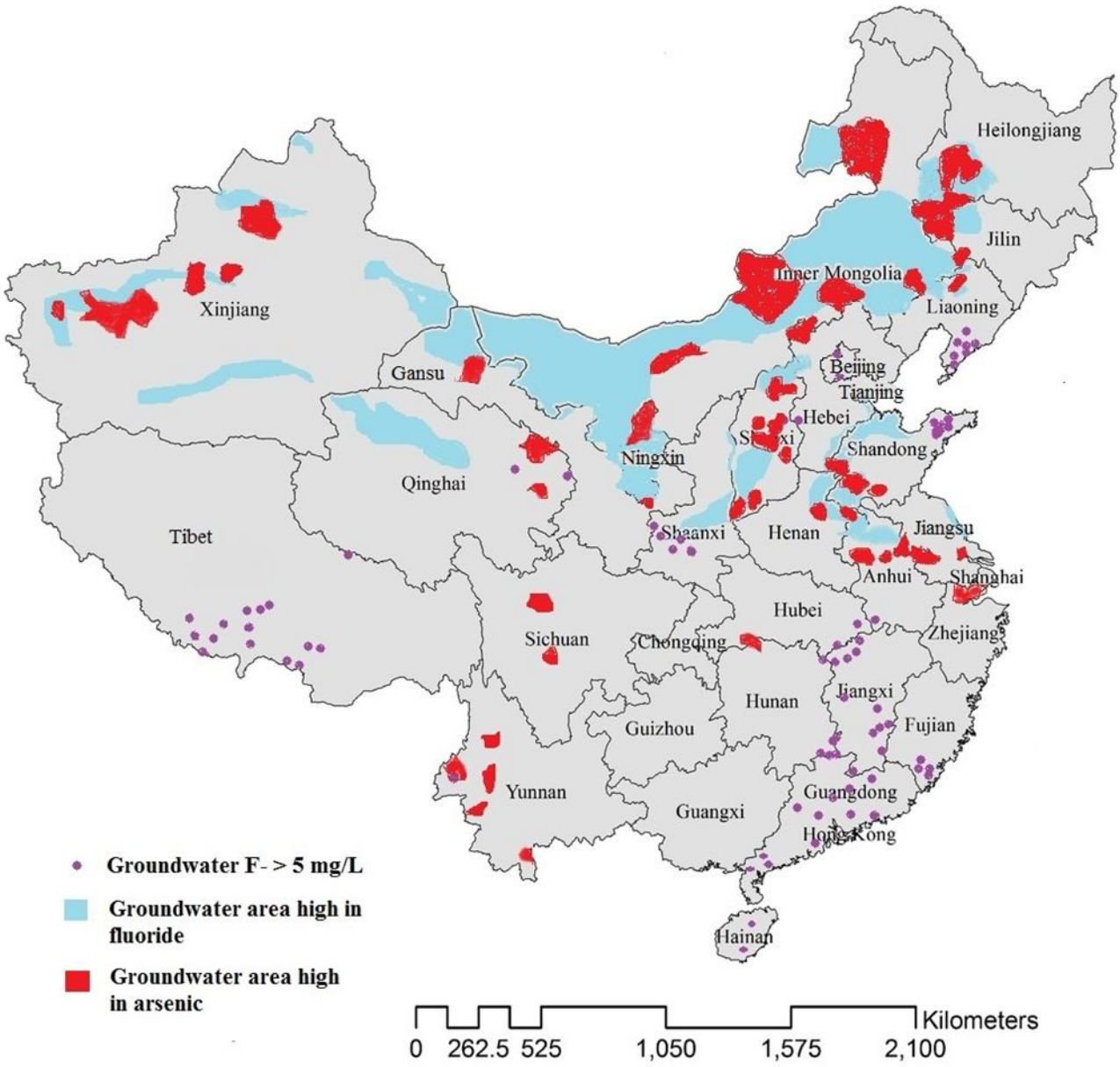

Figure 2.11. Occurrences of high arsenic and fluoride in China's groundwater (Modified from Wen et al., 2013)

Table 2.4. Summary of treatment methods explained in Chapter 2.

Defluoridation Method	Mechanism	Fluoride Removal	Cost	Disadvantages/ Limitations	Location	References
Bone Charcoal	ion exchange	high ; 3.5 mg/l to < 0.2 mg/L F-; 1.4 mg/g adsorption capacity	$2289, $330 or $167 per ton (UK, China, Tanzania)	difficult to make, not sold commercially as much, religious beliefs hinder usage; low regeneration	Thailand & Africa	(Ayoob and Gupta, 2016; Fawell et al., 2006; Dutta et al., 2016; AWWA, 1971)
Activated Alumina (Al_2O_3 grains)	adsorption	high; 8 mg/L F - to 1.5 mg/L F-; surface area 200-300 m^2/g; capacity of 6,750 - 11,760 g F- /m^3 ; 1.08 mg/g adsorption capacity	US $0.975/ kg	treatment depends on pH, optimal pH of 5, effectiveness is reduce to 30-40% after regeneration	South Africa; India, China, Thailand	(Gupta and Ayoob, 2016; Schoeman and MacLeod, 1987; Dutta et al., 2016; RGNDWN, 2001; Daw, 2004)
Clay	adsorption	low, 3 mg/L F- to 1 mg/L F-; 67% removal	low	doesn't have high enough removal for practical use	Sri Lanka	(Gupta and Ayoob, 2016; Fawell et al., 2006).
Eggshells	chemisorption	91 % removal, removes from 7-10 mg/L F- to 1 mg/L F- under optimal conditions (~94% removal), 68 % removal found in other literature	low		India	(Bhaumik et al., 2011; Waghmare and Arfin, 2015; Tantijaroonroj et al., 2009)
Hydroxy-apatite	precipitation of FAP and CaF_2; "surface adsorption" / ion exchange of F- with surface OH- groups; chemisorption	high removal rates: up to 95 % ; 20 mg/L F- to 2.23 mg/L F-; 10 mg/L F- to 1.5 mg/L F-; HAP nanoparticles = 5.5 mg/g adsorption capacity	not affordable yet, esp. for hydroxyapatite nanoparticles	removal rate poor at high pH (> 7.5); removal capacity decreases with regeneration	Mexico, China, India, Saudi Arabia	(Nath and Dutta, 2015; Spinelli et al., 1971; Lin et al., 1981; Li et al., 2010; Jimenez-Reyes and Solache-Rios, 2010; He and Cao, 1996; Poiner et al., 2011; Mourabet et al., 2012; Yu et al., 2013)

Lime	Precipitation	removes from 50 mg/L F- to 9.7 mg/L F-	low	increase of sludge, increase of pH; high residual fluoride (10-20 mg/L F-)	India, China	(Ayoob, 2008; Reardon and Wang, 2000; Wasay et al., 1996; Castel et al., 2000; Huang and Liu, 1999; Islam and Patel, 2007)
Calcium chloride and monosodium phosphate	Precipitation	removal from 10 mg/L F- to 0.4 mg/L	low; \$280/ ton $CaCl_2$ and \$780/ ton MSP	need contact bed (water easily acidic without it), need correct contact time	Africa: Tanzania and Kenya	(Fawell et al., 2006; Dahi et al., 1996; Dahi, 1998; Gupta and Ayoob, 2016)
Alum and Lime (Nalgonda Method)	precipitation, "electrostatic attachment" to flocs	Fluoride Initial: 12.5- 8.8 mg/L F^-; 70% efficiency	US \$0.15 for 7 packets of aluminum sulfate and lime, US \$3.3 for treatment bucket	high alum dosage, residual sulfate and aluminum, hardness of water making water salty, difficult to know how much of the chemicals to add	India, Kenya, Senegal and Tanzania	(Bulusu et al., 1993; Ayoob and Gupta, 2016; COWI, 1998; Dahi et al. 1997; Ayoob et al., 2008; Mjengera and Mkongo, 2003; Fawel et al, 2006; Susheela, 2003; Mohapatra et al., 2009
Limestone with citric and acetic acid	precipitation and adsorption	treated water from 10 mg/L F^- to 1 mg/L F^-	US \$1.56 / kg of acetic acid; US \$1.95 / kg of citric acid; US \$0.012 per liter of water treated for AA; \$ 0.05 per liter for CA		India	(Dutta and Nath, 2010; Dutta et al., 2006; Taher and Ahmed, 2001; Heaman et al., 2002)
Limestone with oxalic acid	precipitation and adsorption	95% removal from initial 10 mg/L	US \$0.007 / kg of limestone; US \$11.03 / kg of oxalic acid; US \$0.14 per liter of water treated	calcium oxalate in treated water	India	(Nath and Dutta, 2012; Das et al., 2007; Yang et al., 1999; Reardon and Wang, 2000; Turner et al., 2005; Holmes and Kennedy, 2000; Bhatt and Paul, 2008)
Limestone with phosphoric acid	precipitation and adsorption	10 mg/L F- down to 0.01 mg/L F-	\$0.00028 per liter of water treated	use of concentrated acids, starts from initial pH of ~1.6	India	(Gogoi et al., 2015; Biswas et al., 2009; Yu et al., 2011; Shan et al., 2009; Dutta et al., 2016)

3. ONSITE DEFLUORIDATION TREATMENT SYSTEMS- CALCIUM CARBONATE ADSORPTION EXPERIMENTS

In many areas of the world, treatment solutions are needed, especially in poor areas where drinking water treatment plants are not available. On-site or individual treatment alternatives can be attractive if constructed from common materials and if simple enough to be constructed and maintained by users. A promising adsorbent is $CaCO_3$. Calcium carbonate is a common chemical that can be found in rocks, such as dolomite, limestone and marble, and seashells, pearls and eggshells. 3.6% of the Earth's crust naturally contains calcium most of which is calcium carbonate (Lutgens and Tarbuck, 2000; Nath and Dutta, 2015). $CaCO_3$ has been shown to defluoridate water through precipitation and adsorption. Broek et al. (2003) determined that using a column filled with granular $CaCO_3$ could be used as a post treatment for wastewater to remove fluoride from 8 mg/L down to 0.6 mg/L. Turner et al. (2005) showed that when F^- comes into contact with calcium carbonate, an instant F^- adsorption occurs and calcium carbonate dissolves. Dissolution of calcium carbonate increases calcium concentration until saturation is reached and CaF_2 precipitation occurs.

For our experiment, we believe the mechanism of F^- removal is ion exchange physical adsorption. Precipitation of CaF_2 occurs only at higher concentrations, 10 to 20 mg/L F^- or more due to the solubility product of CaF_2 ($3.4 * 10^{-11}$ at 25 ^{o} C) (Gupta and Ayoob, 2016; Nath and Dutta, 2010; Ebbing and Gammon, 2009). Adsorption is the adhesion or concentration of substances at a surface or interface. The mechanism can either be "physisorption", "chemisorption" or both. Physical adsorption is caused by van der Waals forces and the adsorbed

molecule is not fixed to a certain site at the surface but is free to move translationally within the interface. Chemisorption occurs when the adsorbate and the adsorbent go through chemical interaction and the adsorbed molecules are not "free to move on the surface or within the interface." Chemisorption is a stronger bond compared to physisorption. Ion exchange is another type of adsorption frequently denoted as "exchange adsorption" where "ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface." The ions held by electrostatic forces on the surface of a solid are exchanged with ions of similar charge on the solid which is immersed. Ion exchange is considered a sorption process because the exchange of ions from the charged functional groups occurs at the surface of the solid and because the ions "undergo a phase transfer from solution phase to surface phase." Most adsorption processes are a combination of the three categories of adsorption (Weber, 1972; Gupta, 2008).

By comparing different adsorbents, such as commercial resins, seashells, eggshells and calcium pills, we have found that calcium carbonate in certain physical states (e.g. as a very fine powder) has comparable fluoride removal abilities to the commercial resins that have been optimized for fluoride removal. Though there have been experiments performed already by other researchers on calcium containing materials ($CaCl_2$, $Ca(OH)_2$, $Ca(NO_3)_2$, $Ca_5(PO_4)_3$) , CaO, $CaCO_3$), our objective is to develop a simple defluoridation system for potable water that requires no special operational expertise or the use of hazardous chemicals, and can be operated by the local people (Bhaumik et al., 2012; Nath and Dutta, 2015; Jimenez Reyes and Rios, 2010; Yang et al., 1999; Ben Nasr et al., 2011; Bhargava and Killedar, 1991; Christoffersen et al., 1984).

3.1 Materials and Methods

3.1.1 Materials

Fluoride solutions were obtained by diluting a 1,000 mg/L NaF ACS reagent grade standard solution from Ricca Chemical Company, USA. Powdered ACS reagent grade calcium carbonate was purchased from Thermo Fisher Scientific, USA, Sigma Aldrich, USA and MP Biomedicals, USA. Samples were measured in 50 mL plastic Falcon tubes that were obtained from Thermo Fisher Scientific, USA. SIR 900 and SBG2 synthetic resins were obtained from Resintech, USA, and Amberlite IRA 400 synthetic resins were obtained from Rohm and Haas, USA. Eggshells, calcium pills, and seashells were obtained from local stores. Eggshells and seashells were air dried and then ground to a powder using a blender. The approximate particle sizes of the calcium carbonate were 100 µm. DI water was used for all the experiments.

3.1.2 Instrumental Analysis

Fluoride concentrations were determined using a Thermo Scientific Orion Versa Star Advanced Electrochemistry Meter and a Thermo Scientific Orion 9609 BNWP Ion Plus Sure-Flow Fluoride ion selective electrode, with an accuracy percentage of 98 % (OI Analytical, 2014, Thermo Scientific, 2011). TISAB II from Thermo Scientific was used to maintain high, constant ionic strength, adjust the pH, and complex interfering species. Lab-line Instruments Inc. Environ-Shaker 3597 was used to shake the samples.

3.1.3 Methods of Batch and Isotherm Experiments

Isotherm experimental conditions were chosen to match conditions needed to produce safe drinking water. We compared isotherms between different adsorbents: Resintech SIR 900,

Resintech SBG2 Rohm and Haas Amberlite IRA 400, eggshell powder, seashell powder, calcium pill powder, and calcium carbonate. We placed varying amounts of the adsorbents into 50 mL Falcon tubes and added 20 mL of 10 mg/L fluoride solution. We then shook the samples for 1 hour at 100 rpm and measured the fluoride concentrations using the Thermo Scientific Electrochemistry Meter and Fluoride ion selective electrode. The amount of fluoride adsorbed by the adsorbents (x/m) was calculated and graphed with the corresponding concentration of fluoride. x/m (mg/g) values were calculated using the equation below:

$$x/m = (C_0 - C_t)V/m \quad (1)$$

where C_0 (mg/L) is the initial fluoride concentration, C_t (mg/L) is the concentration of fluoride at time t, V is volume of the solution (L), m is the mass of adsorbent used (g) and x is the mass of fluoride adsorbed (mg).

A Freundlich isotherm was performed for calcium carbonate using the equation below:

$$\ln q = \ln (K) + \frac{1}{n}\ln(C) \quad (2)$$

where q (mg/g) is the adsorption capacity , C is the concentration of fluoride (mg/L) and K is a constant. Ln(q) was plotted against ln(C) to determine the slope, which is $\frac{1}{n}$.

A Langmuir isotherm was performed using the equation below:

$$\frac{1}{q} = \frac{1}{b*q_m} * \frac{1}{C} + \frac{1}{q_m} \quad (3)$$

where q (mg/g)is the adsorption capacity, C is the concentration of fluoride, qm is theoretical qmax (mg/g), b is a constant. $\frac{1}{q}$ is plotted againt $\frac{1}{C}$ to determine b and q_m.

A Dubinin-Radushkevich (D-R) isotherm was also performed to determine the mechanism for adsorption using the equations below:

$$\ln q = \ln q_m - K_D \varepsilon^2 \quad (4)$$

$$\varepsilon^2 = RT\ln(1 + \frac{1}{C}) \quad (5)$$

where q is the adsorption capacity (mg/g), qm is maximum adsorption capacity (mg/g), Ɛ is the Polanyi potential, C is the concentration (mg/L), K_D ($\frac{mol^2}{kJ^2}$) is the activity coefficient that can be used to calculate the mean free energy E_s (kJ/mol). If Es is between 8 and 16 kJ/mol, it means that the main mechanism is chemisorption. If Es is below 8 (kJ/mol), it means the driving mechanism is physical adsorption. lnq was plotted against ε^2 to determine q_m and K_D (Bhaumik et al., 2012; Gogoi and Dutta, 2016).

$$E_s = \frac{1}{\sqrt{2K_D}} \quad (6)$$

3.1.4 Methods for Selectivity Experiments

Selectivity experiments were tested on SIR 900 and calcium carbonate. An isotherm experiment similar to the isotherm experiments described above was performed except that varying amounts of sodium chloride were added, corresponding from 0 to 100 mg/L Cl^- concentration. Four batch studies were performed for SIR 900 media added at 0.7 & 2.0 grams. For calcium carbonate, 1 gram was added at increasing amounts of Cl^-. x/m values (amount of fluoride adsorbed by the media) were plotted against mg/L Cl^-.

3.1.5 Methods for Equilibrium Experiments

The time for the samples to reach equilibrium was determined. Varying amounts of calcium carbonate (0.11g, 0.21 g, 0.4 g, 0.57 g) were placed into 1,000 mL Erlenmeyer flasks and filled with 5.6 mg/L of fluoride solution. We then shook the samples for 403 minutes at 100 rpm using Lab-line Instruments Inc. Environ-Shaker 3597 and removed aliquots from the Erlenmeyer flasks for analysis at different time intervals. We measured the fluoride concentrations using the ion selective electrode and graphed concentration of fluoride versus time.

For the second set of equilibrium experiments, we tested various calcium carbonates (MP Biomedicals, Thermo Fisher, and commericial pill) using 0.3 grams. The different brands of calcium carbonate were put in 50 mL Falcon tubes and shaken using Barnstead Thermolyne Labquake Shaker Rotisserie PAT.NO. 3,625,485 for 0 to 24 hours. We measured the fluoride concentrations using the ion selective electrode and graphed concentration of fluoride versus time.

3.1.6 Methods for Column Experiments

A single column experiment was performed followed by a series column experiment consisting of 3 columns. Water containing 5 mg/L of fluoride for the single column experiment and 7 mg/L for the column in series experiment was pumped in an up flow direction through the columns using Cole-Palmer Masterflex Microprocessor Pump at approximately 0.43 mL/min for single column and 0.37 mL/min for column in series. The columns were 2.5 cm in diameter and 35 cm long, containing approximately 95 grams of Thermo Fisher Scientific $CaCO_3$ and approximately 95 grams of Teflon beads. Teflon beads were used as a bulking agent. Glass wool was used at both ends of the column to keep the calcium carbonate and Teflon beads in place. Samples of the water from each column were taken at different time intervals, and fluoride concentrations were determined. x/m (mg of fluoride adsorbed/ g of calcium carbonate) values were calculated. Equations 4 and 5 were used to calculate x/m values for a single column and column in series.

$$\text{Single Column : } \frac{x}{m} = \sum_0^t Q \frac{Co - C_t}{m} \tag{7}$$

$$\text{Column in Series: } \frac{x}{m} = \frac{\Sigma \quad \left(\sum_0^t Q\frac{Co-C1}{m_1} + \sum_0^t Q\frac{C_1-C_2}{m_2}\sum_0^t Q\frac{C_2-C_3}{m_3}\right)}{number\ of\ columns} \tag{8}$$

where Q is the flow rate (mL/min), Co is the initial concentration of fluoride, C_t is the concentration of fluoride at time t and m is the amount of adsorbent used (g).

3.2 Results and Discussion

3.2.1 Batch & Isotherm Experiment for Different Adsorbents

Figure 3.1 shows x/m (mg/g) values of different adsorbents plotted against fluoride concentration to compare experimental isotherms for each of the adsorbents. The Freundlich and Langmuir isotherms lines are also shown in Figure 3.1. Table 3.1 shows different adsorption values for the 10 adsorbents used at 1.5 mg/L. Table 3.2 shows the coefficients calculated for the Freundlich, Langmuir and Dubinin-Radushkevich isotherms. Through the D-R isotherm, we calculated the Es mean free energy as 0.845(kJ/mol) showing that the main adsorption process is physical adsorption. We used synthetic commercial resins as a benchmark to compare to for the calcium containing adsorbents. Though SIR 900 (0.08 mg/g) and the commercial calcium pill (0.065 mg/g) had the highest adsorption capacity, using these adsorbents would not be practical in developing countries due to cost. Calcium carbonate would be the next best chemical with adsorption capacity of 0.035 mg/g. From this isotherm, it is clear that superficial surface area of the adsorbent is important. Both blended $CaCO_3$ showed better adsorption capacity than unblended $CaCO_3$, and powdered eggshell showed better adsorption capacity than grounded eggshell. We believe that the reason the first commercial calcium pill had such high adsorption capacity is due to its small grain size (a very fine powder), which increases surface area. From Table 3.2, we can see that as particle size of the media decreased, adsorption capacity increased. Note also that lowering pH of the waters would improve defluoridation of the system using $CaCO_3$ because it would create more dissolution of $CaCO_3$, which would mean the presence of more Ca^{2+} ions, saturation of the solution, and precipitation of CaF_2. Theoretically, you could remove almost all the fluoride if pH levels are low enough (Turner and Binning, 2005; Yang et

al., 1999). pH for $CaCO_3$ batch experiments were approximately 9.63-10.19, which would be too high for drinking water (Figure 3.2). After mixing the solution with a magnetic stirrer, allowing exposure to the atmosphere, pH was brought down to approximately 7.8. pH control is likely beyond the expertise of an on-site home treatment system in developing countries. Finding a method of pH reduction without using advanced technology or commercial chemicals should be a topic of future research.

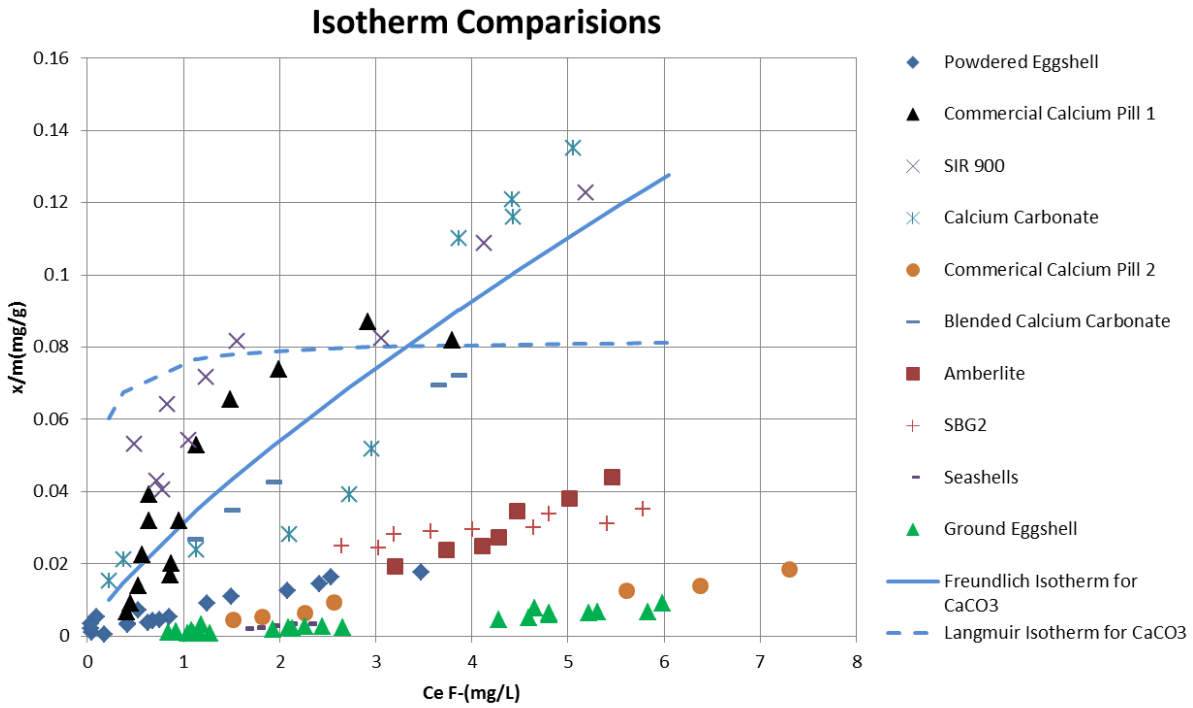

Fig. 3.1. Adsorption capacity versus fluoride concentration among commercial resins and calcium containing adsorbents with Freundlich and Langmuir isotherms. Commercial resins (SIR 900, Amberlite, SBG2) are ion-exchange resins.

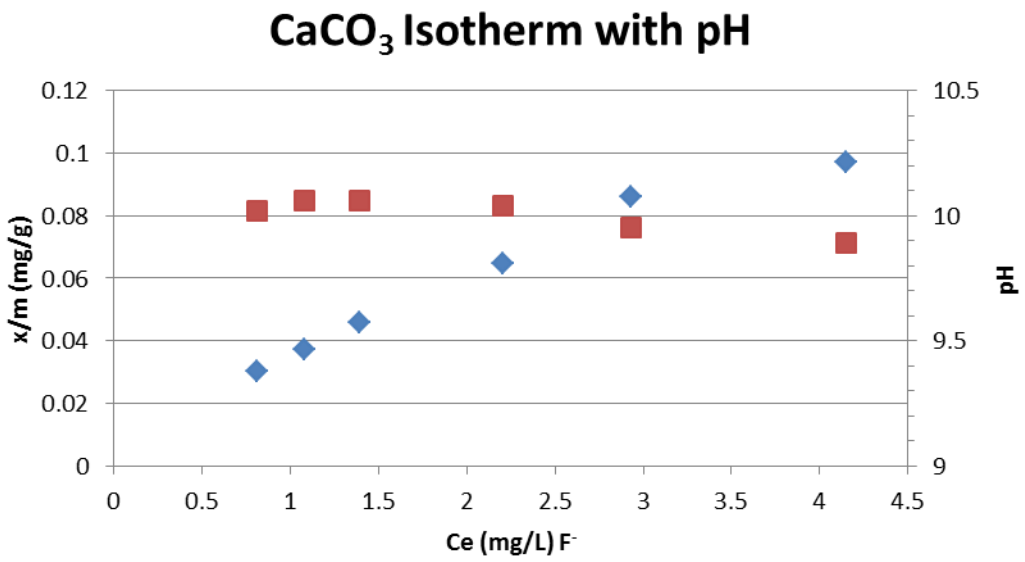

Fig. 3.2. Adsorption capacity and pH versus fluoride concentration for $CaCO_3$

Table 3.1. Table of x/m (mg/g) adsorption capacity values at 1.5 mg/L F^- for commercial resins and forms of calcium carbonate

Adsorbent	**x/m (mg/g) at 1.5 mg/L F^-**
SIR 900	0.08
Commercial Calcium Pill 1	0.065
Blended Calcium Carbonate	0.035
Unblended Calcium Carbonate	0.026
SBG2	0.019
Powdered Eggshells	0.012
Amberlite IRA 400	0.005
Commercial Calcium Pill 2	0.0046
Seashells	0.0017
Ground Eggshells	0.00095

Table 3.2. Particle size versus adsorption capacity. As particle size increases, adsorption capacity decreases.

Media	approximate particle size (mm)	x/m at 1.5 mg/L F- (mg/g)
commercial calcium pill	0.0033	0.065
reagent grade calcium carbonate	0.0050	0.026
powdered eggshell	0.0067	0.012
seashell	1.0	0.0017
eggshell	1.3	0.00095

Table 3.3. Calculated isotherm constants for Freundlich, Langmuir and Dubinin-Radushkevich isotherm models

Freudlich Isotherm Values		
K	n	
0.03	1.29	
Langmuir Isotherm Values		
qm (mg/g)	b	
0.082	0.9	
Dubinin- Radushkevich Isotherm Values		
qm (mg/g)	K_D (mol^2/kJ^2)	Es (kJ/mol)
0.12	0.7	0.845

3.2.2 Calcium Carbonate Experiments

Selectivity experiments using calcium carbonate and SIR 900 showed negligible impact of chloride on fluoride adsorption. With increasing concentrations of Cl^-, adsorption capacity did not change much (Figure 3.3 and 3.4). This is important to note because if competing anions reduce removal rates significantly, it will render the treatment system less effective. For the equilibrium experiment, we plotted concentration of fluoride against time for different amounts of calcium carbonate (0.1g, 0.2g, 0.4 g and 0.56 g). We found that the equilibrium time occurred at approximately 180 minutes (Figure 3.5) and at one hour, approximately 77% of the equilibrium concentration is achieved (Figure 3.6).

For the single column study, we graphed C/C_0 (concentration of fluoride/ initial concentration of fluoride) at different time intervals, and found that the fluoride concentration was at 1.5 mg/L at approximately 166 minutes. 72.3 mL of water could be treated with a single column using approximately 95 grams of calcium carbonate (Figure 3.7). We would need 2.6 kg of calcium carbonate to attain 2 liters of defluoridated water, which is the average amount of water a person would drink per day. pH was approximately 8.6, which would be permissible for drinking water.

We tried to improve the effectiveness of the treatment system by putting three columns in series. We plotted C/C_0 at different time intervals, and found that for the ending effluent column at 1.5 mg/L of fluoride, the x/m value was 0.61 mg/g, time was 906 minutes, and volume of water treated was 336 mL. For the middle column at 1.5 mg/L of fluoride, the x/m value was 0.15 mg/g. time was 599 minutes and volume of water treated was 222 mL. For the beginning influent column at 1.5 mg/L of fluoride, the x/m value was 0.0091 mg/g, time was 149 minutes

and volume of water treated was 55.3 mL (Figure 3.8). x/m for the entire column system was 0.38 mg/g, which is close to the x/m value we attained in the isotherm experiment. We would need 1.67 kilograms of calcium carbonate to attain 2 liters of defluoridated water having an initial concentration of approximately 7 mg/L.

The advantage of this treatment system is that $CaCO_3$ is an abundant, accessible chemical in the world. Limestone is inexpensive and is estimated to cost US $ 0.007/kg in India, but varies by location. Therefore, is not possible for us to generally predict costs. Cost estimates will have to be made for specific locations. The disadvantage of this treatment system is the use of a lot of $CaCO_3$, and the cost of disposal. Lowering pH and reducing particle size would increase removal efficiency. Reuse and regeneration may also be an option. Dutta et al. (2015) found a 50% regeneration of removal efficiency after simple scrubbing of limestone, soaking with NaOH or $Ca(OH)_2$. Additionally, this treatment system can be used as a pre-treatment to reduce higher concentrations of fluoride or when treating lower concentrations of fluoride at 5 mg/L F^- or less. This would reduce the amount of $CaCO_3$ needed.

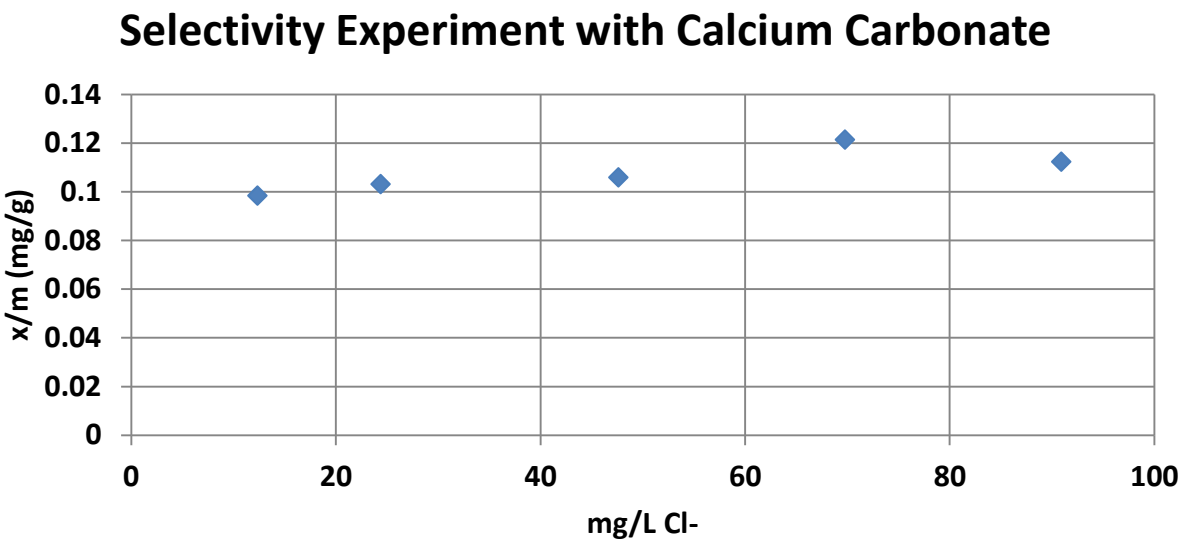

Fig. 3.3. Calcium carbonate selectivity experiment analyzing impact of the presence of Cl- for defluoridation

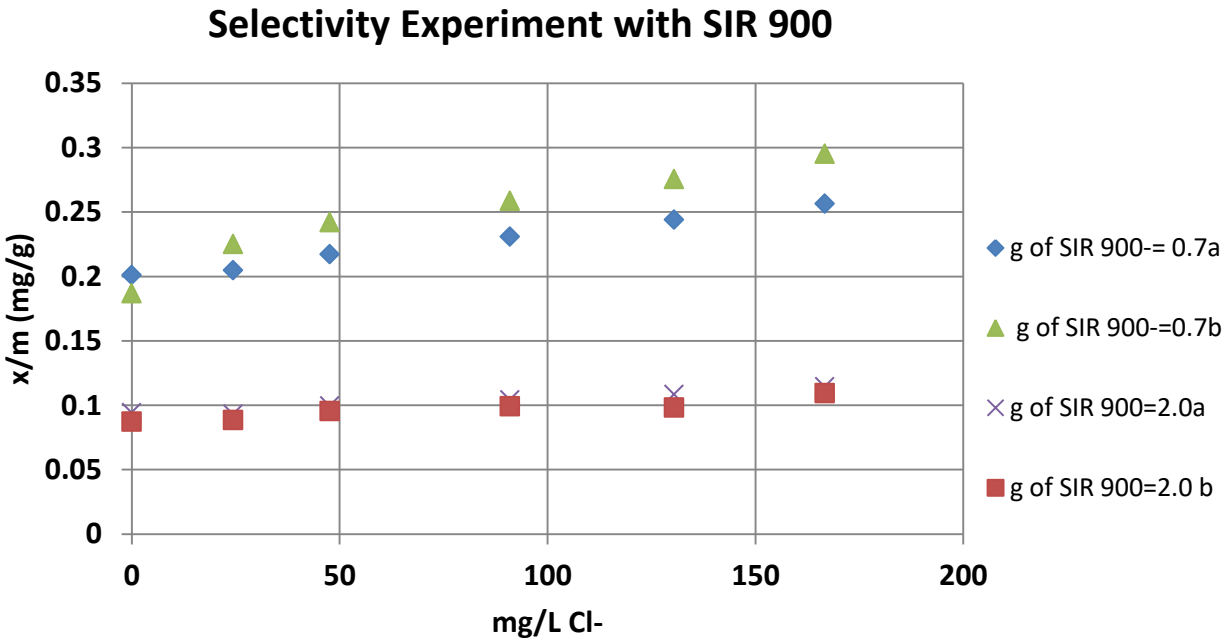

Fig. 3.4. SIR 900 selectivity experiment analyzing impact of the presence of Cl- for defluoridation

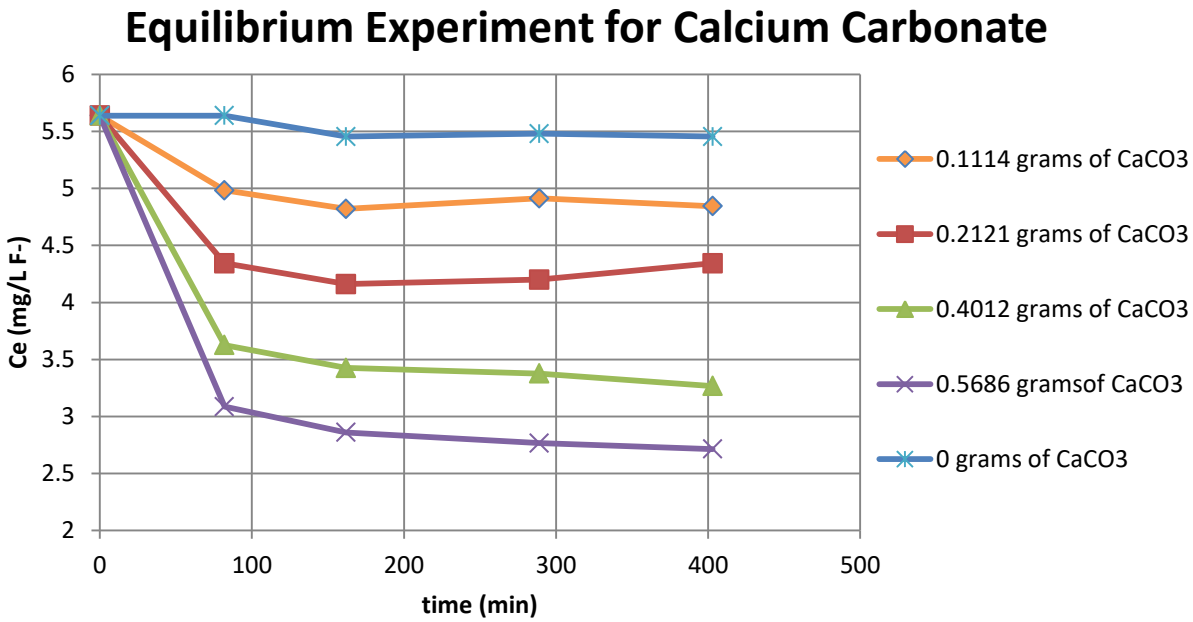

Fig 3.5. Equilibrium experiment for defluoridating water using different amounts of calcium carbonate plotting concentration F^- (mg/L) versus time (min)

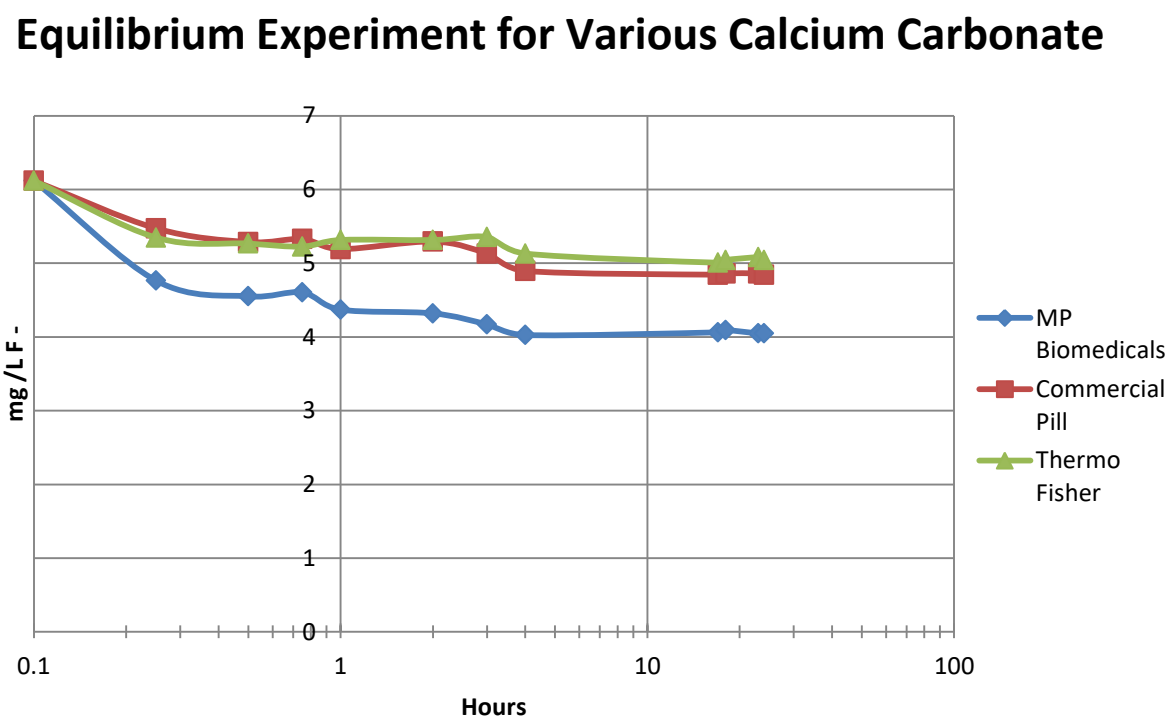

Fig 3.6. Equilibrium experiment for various calcium carbonate using 0.3 grams. Fluoride concentration is approximately 77% of equilibrium fluoride concentration at 1 hour.

3.3 Conclusions

Excessive fluoride in drinking water has severe consequences to a person's health and has adversely affected many people around the world. Since many areas in the world do not have the resources to have centralized water treatment systems or expensive technology to defluoridate water, there is a need for an onsite defluoridation system that is inexpensive, doesn't involve hazardous materials, uses materials that are readily accessible, and is maintainable by users. In this study, we looked at different adsorbents to use in our defluoridation system. We compared different forms of calcium carbonate to commercial synthetic resins. We chose to further study on granular calcium carbonate, since SIR 900 and calcium pills cannot be used in developing countries due to cost. $CaCO_3$ can bring fluoridated water (below 10 mg/L F^-) down to drinkable fluoride concentrations (below 1.5 mg/L) via physical adsorption, which we determined through D-R isotherm calculations. In our batch studies, we determined that the x/m value for calcium carbonate was 0.035 mg/g at 1.5 mg/L F^- and that the equilibrium time was at approximately 180 minutes. At one hour, approximately 77% of the equilibrium concentration is achieved. In the column studies, we determined that the x/m value for the single column study was 0.011 mg/g and 0.038 mg/g at 1.5 mg/L F^- for the column in series study. A person would need to use 1.67 kilograms of calcium carbonate to defluoridate 2 liters of water per day. This is a lot of $CaCO_3$ to be used, but the amount may be lowered through regeneration and reuse by simple scrubbing. Other options can be lowering pH and reducing particle size, as well as using this treatment as a pre-treatment defluoridation step or for waters that have 5 mg/L F^- or less. Further studies need to involve finding nonhazardous methods to improve adsorption capacity, such as using phosphate containing materials and lowering pH. Through this study, we can be a step closer to providing an accessible onsite defluoridation treatment system to places in need.

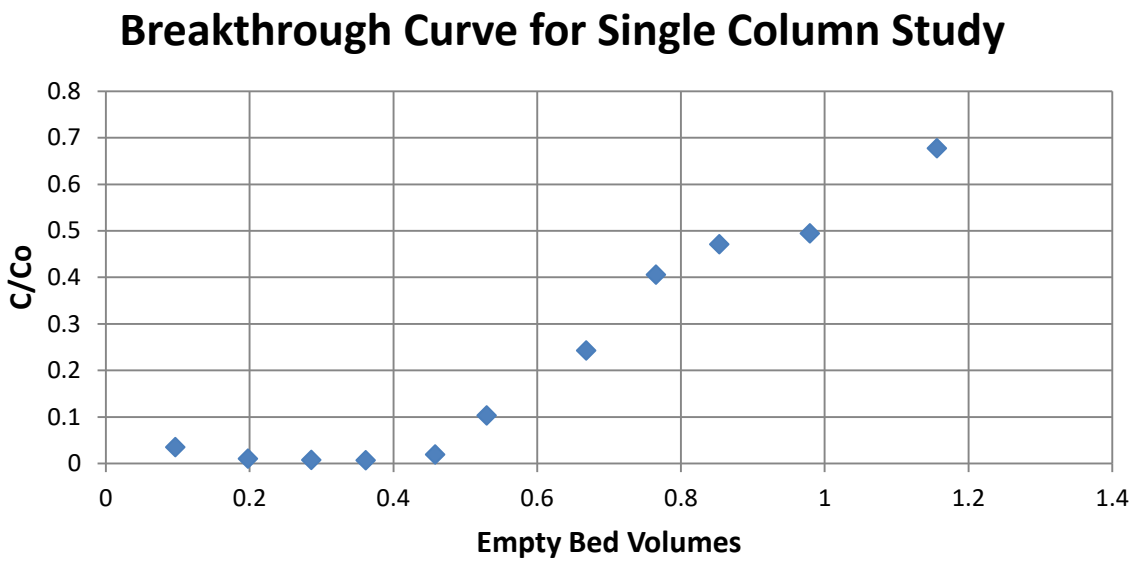

Fig. 3.7. Breakthrough curve using a single column containing calcium carbonate plotting C/Co versus empty bed volumes.

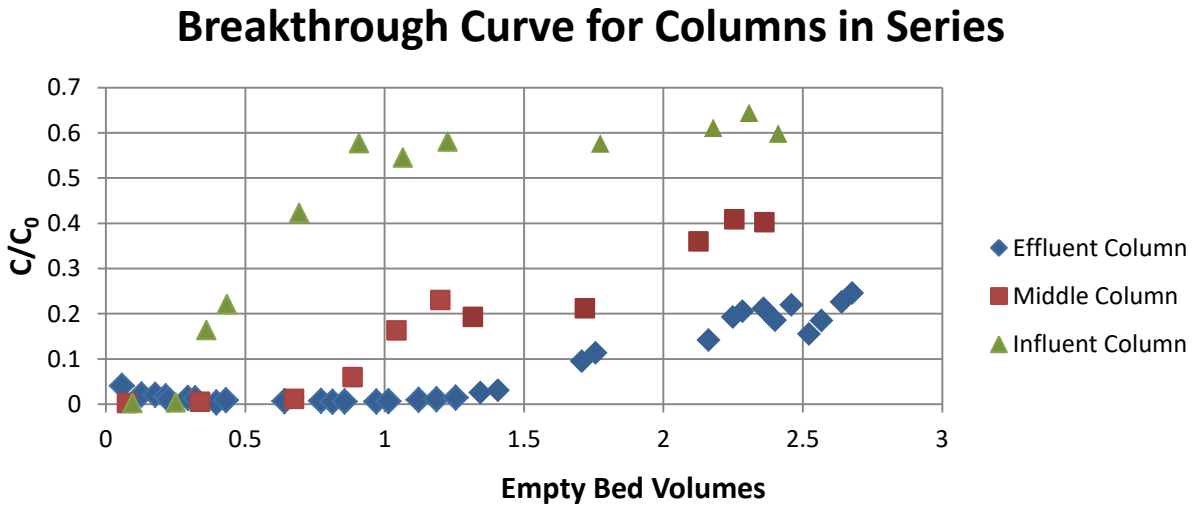

Fig. 3.8. Breakthrough curve using columns in series containing calcium carbonate plotting C/Co versus empty bed volumes

4. ONSITE DEFLUORIDATION TREATMENT SYSTEMS- CALCIUM PHOSPHATE REMOVAL SYSTEMS

Although we can defluoridate water down to drinkable fluoride concentrations through adsorption with calcium carbonate, there are significant limitations, such as low adsorption capacity and the large amount of calcium carbonate needed. Therefore, we need to find other nonhazardous materials that can defluoridate water and improve the current proposed treatment system described in Chapter 3. There have been several studies on defluoridating water using different calcium containing materials ("bone char", slack lime, $CaCl_2$, $Ca(NO_3)_2$, $CaSO_4$, cement paste) (Waghmar and Arfin, 2015, Nath and Dutta, 2015). Reardon and Wang (2000) reduced fluoride concentrations from 10-25 mg/L down to below 2 mg/L by adding CO_2 in the water before treating it through two limestone columns in series. Influent pH was 4.97 which helped with dissolution of $CaCO_3$.

Calcium phosphate systems have also been studied. He and Cao (1996) studied different calcium phosphate systems (brushite, monocalcium phosphate, tricalcium phosphate, hydroxyapatite, calcium chloride, calcium hydroxide, calcium carbonate, bone char, potassium dihydrogen phosphate, calcium lactate, fluorhydroxyapatite), and found that if we can use only one material, tricalcium phosphate (87%) would have the best removal rate followed by hydroxyapatite (68 %), followed by bone char (66.4%). The best combination of the materials would be bone char and monocalcium phosphate, which could defluoridate 100 mL of water from 10.4 mg/l F^- to 0.6 mg/l F^- with 300 mg of bone char and 23 mg of monocalcium phosphate. Adler and Klein (1938) treated potable fluoridated water using tricalcium phosphate and determined that 1 kg of tricalcium phosphate could remove 6.05 grams of fluoride, and regeneration was possible by washing the adsorbents with sodium hydroxide followed by

hydrochloric acid. Turner et al. (2010) used potassium phosphate with calcite to defluoridate water. Adding 17 mg/L of potassium phosphate decreased fluoride concentrations by 20 %. Adding 500 mg/L of potassium phosphate removed almost all the fluoride present. The calcite precipitated with phosphate to form fluorite, fluorapatite and hydroxyapatite. Gogoi et al. (2015) studied defluoridation using limestone and phosphoric acid. By adding phosphoric acid, the adsorption capacity increased from 0.39 mg/g (limestone alone) to 1.10 mg/g. The mechanisms proposed were precipitation of fluorite and calcium phosphate hydroxide, and adsorption of fluoride with hydroxyapatite forming fluorapatite.

From this literature review, we wanted to look at different calcium and phosphate systems to determine the best combination of calcium and phosphate materials that had good fluoride removals but would be able to be used practically in developing countries. We believed that this would be a good direction to research because of the effective fluoride removal from calcium phosphate systems found in literature review and the fact that the solubility product of hydroxyapatite $Ca_5(PO_4)_3(OH)$ (2.91×10^{-58} at 25 ºC) and fluorapatite $Ca_5(PO_4)_3F$ ($8.6 * 10^{-61}$ at 25 º C) are so low compared to the solubility product of fluorite (CaF_2, $3.4 * 10^{-11}$ at 25 º C), making the precipitants extremely insoluble and easy to precipitate (Bell et al., 1978; McCann, 1968; Ebbing and Gammon, 2009).Primary aspects we were concerned about were the accessibility of the materials, and not using hazardous materials that would be dangerous for the local people to use.

4.1 Methods and Materials

4.1.1 Materials

Fluoride solutions were obtained by diluting a 1,000 mg/L NaF ACS reagent grade standard solution from Ricca Chemical Company, USA. Powdered ACS reagent grade calcium carbonate was purchased from Thermo Fisher, USA, Sigma Aldrich, USA and MP Biomedical, USA. Phosphoric acid (85% w/v H_3PO_4), HCl (0.1 M), and ACS reagent grade K_2HPO_4 were obtained from Thermo Scientific, USA. Samples were measured in 50 mL plastic Falcon tubes that were also obtained from Thermo Fisher Scientific, USA. Erlenmeyer flasks were used for samples greater than 50 mL. Eggshells and seashells were obtained from local stores, air dried and then ground to a powder using a blender. The approximate particle size of the calcium carbonates were 100 µm. DI water was used for all the experiments.

4.1.2 Instrumental Analysis

Fluoride concentrations were determined using a Thermo Scientific Orion 420A+ basic pH/mV/ORP Meter and a Thermo Scientific Orion 9609 BNWP Ion Plus Sure-Flow Fluoride ion selective electrode. TISAB II from Thermo Scientific was used to maintain high, constant ionic strength, adjust the pH, and complex interfering species. Burrell Scientific wrist action shaker model 75 was used to shake the samples for 1 hour and Barnstead Thermolyne Labquake Shaker Rotisserie PAT.NO. 3,625,485 was used to shake the samples for approximately 15 minutes with TISAB II afterwards. A Thermo Scientific Orion 3 Star pH portable meter was used to measure pH. Fisher Scientific Thermix Magnetic Stirrer Model 120 MR was used to stir volumes of water greater than 50 mL.

4.1.3 Methods of KH_2PO_4 Experiments

We wanted to determine the effects of adding K_2HPO_4 to $CaCO_3$, hoping that it would improve adsorption capacity. We placed increased amounts of K_2HPO_4 (0.1 -3.3 grams) with 2 grams of $CaCO_3$ for each sample. The samples were put in 50 mL Falcon tubes and 20 mL of 5 mg/L of fluoride were added into each sample. We then shook the samples for 1 hour using the Burrell Scientific wrist shaker and measured the fluoride concentrations using the Thermo Scientific Electrochemistry Meter and Fluoride ion selective electrode. The amount of fluoride removed by the media (x/m) was calculated and graphed with the corresponding amount of K_2HPO_4 (g) used. x/m (mg/g) values were calculated using the equation below:

$$x/m = (C_0 - C_t)V/m \quad (4.1)$$

where C_0 (mg/L) is the initial fluoride concentration, C_t (mg/L) is the concentration of fluoride at time t, V is volume of the solution (L), m is the mass of media used (g) and x is the mass of fluoride removed (mg) (Figure 4.1).

We wanted to bring the pH of the solution down to improve removal efficiency of fluoride by adding HCl. We added enough HCl to bring the pH down to 1.88 and 1.02. 22 mL of 0.1 M HCl was used to bring the solution down to 1.88. The rest of the experiment was done the same as previously described with the addition of adding increasing amounts of K_2HPO_4 (g) in each sample and determining the adsorption capacity of $CaCO_3$. We then plotted amount of K_2HPO_4 (g) against adsorption capacity of $CaCO_3$ to see if adding HCl to the samples improved adsorption capacity of $CaCO_3$ (Figure 4.2).

4.1.4 Methods of $CaCO_3$ with Phosphoric Acid

Given that the experiments with K_2HPO_4 did not have positive results, we moved onto adding phosphoric acid to $CaCO_3$. We did two sets of experiments with 4 grams of $CaCO_3$ and 0.02 grams of $CaCO_3$. We added different amounts of H_3PO_4 to bring the solution down to various pHs ranging from 1-8. We plotted pH against adsorption capacity of $CaCO_3$ to determine if adding H_3PO_4 would improve defluoridation removal rates and at what pH would the solution need to be to improve adsorption capacity of $CaCO_3$ (Figure 4.3)

We compared isotherms for different brands of $CaCO_3$ (MP Biomedicals, Sigma Aldrich and Thermo Fisher) with Thermo Fisher $CaCO_3$ plus H_3PO_4. We placed varying amounts of the adsorbents into 50 mL Falcon tubes and added 20 mL of various fluoride concentrations (5-10 mg/L). For the Thermo Fisher $CaCO_3$ plus H_3PO_4 samples, 0.78 mL of phosphoric acid (85% w/v) was added to the samples to make the initial pH approximately 1. We then shook the samples for 1 hour using the Burrell Scientific wrist shaker and measured the fluoride concentrations using the Thermo Scientific Electrochemistry Meter and Fluoride ion selective electrode. The amount of fluoride adsorbed by the adsorbents (x/m) was calculated and graphed with the corresponding concentration of fluoride. We then graphed x/m (mg/g) against concentration of F^- for $CaCO_3$ (MP Biomedicals, Sigma Aldrich and Thermo Fisher) and Thermo Fisher $CaCO_3$ plus H_3PO_4 (Figure 4.4).

Additionally, we wanted to determine if adding phosphoric acid to all sources of $CaCO_3$ would work, such as eggshells and seashells. We added 0.78 mL of phosphoric acid (85% w/v) with 5 mg/L F^-. We then added increasing amounts of $CaCO_3$, eggshells and seashells into the

samples. Fluoride concentrations were determined by using the Thermo Scientific Electrochemistry Meter and Fluoride ion selective electrode. Grams of eggshells, seashells and $CaCO_3$ were graphed against concentration of F^- (Figure 4.5).

4.1.5 Methods of Different Calcium Phosphate Systems

We wanted to compare different calcium phosphate systems to find the optimum most effective fluoride removal rates. Another major goal was to find a calcium phosphate system that did not use hazardous chemicals such as concentrated acids. We used different calcium and phosphate chemicals: $CaCl_2$, $Ca(OH)_2$, limestone rock ($CaCO_3$) , and NaH_2PO_4, and H_3PO_4. Table 4.1 shows the combinations of calcium and phosphate chemicals, as well as the amounts of each used. Samples were put in 50 mL Falcon tubes and shook for one hour using a wrist shaker. Fluoride concentrations and final pHs were determined. Initial concentration of fluoride was approximately 5 mg/L F^-.

4.1.6 Slaked Lime $Ca(OH)_2$ and Monosodium Phosphate (NaH_2PO_4) Experiments

After comparing different calcium phosphate systems, we determined that slaked lime and monosodium phosphate were the best combination of calcium and phosphate chemicals to use. We chose this combination because slaked lime and monosodium phosphate had effective fluoride removal, could easily dissociate in water without the use of acids, and didn't have such low pHs found when using $CaCl_2$. We put 20 mL of 5 mg/L F^- in 50 mL falcon tubes and did two sets of experiments, one with 1 gram of monosodium phosphate and one with 2 grams of monosodium phosphate. We added increasing amounts of slaked lime in the fluoridated water and shook the samples for one hour with the wrist shaker. Resulting concentration of fluoride was determined and we plotted grams of slaked lime against concentration of fluoride (Figure 4.6).

We found that fluoride concentration removal increased with the increase of NaH_2PO_4 (Table 4.1) and that adding more $Ca(OH)_2$ didn't help with increasing fluoride removal and at a certain point even hindered fluoride removal (Figure 4.6). We found that in order to get the resulting water to be a neutral pH of~7, amount of $Ca(OH)_2$/amount of NaH_2PO_4 should equal to approximately 0.45. We tested on 0.45 grams of slaked lime and 1 gram of NaH_2PO_4 and the maximum volume and initial fluoride volumes these chemicals could treat. We measured different volumes of 5 mg/L of fluoride (100- 1,000 mL) in Erlenmeyer flasks, put 0.45 grams of $Ca(OH)_2$ and 1 gram of NaH_2PO_4 in the flasks. We then used a Fisher Scientific magnetic stirrer for one hour and measured fluoride concentrations. Volume of water (mL) was plotted against fluoride removal ratio C/C_0. We also tested how high of an initial fluoride concentration these chemicals could treat. Increasing amounts of fluoride concentrations were diluted (10-100 mg/L F^-) from a 1,000 mg/L F^- stock solution. 20 mL of varying amounts of fluoride concentrations (10-100 mg/L) were put into Falcon tubes. 0.45 grams of $Ca(OH)_2$ and 1 gram of NaH_2PO_4 were added into the samples and shaken for an hour using a wrist shaker. Resulting fluoride concentration was determined and percentage removal was calculated (Table 4.2)

4.6.1.1 Slaked Lime and Monosodium Phosphate Experiments with Stoichiometry

We wanted to determine the least amount of slaked lime and monosodium phosphate needed to remove all the fluoride in solution. To do this, we evaluated the chemical equations and mechanisms occurring. A proposed reaction scheme are as follows:

$$NaH_2PO_4 \cdot H_2O \rightarrow Na^+ + 2H^+ + PO_4^{3-} + H_2O \quad (4.1)$$

$$H_2PO_4^- + Ca(OH)_2 \rightarrow Ca^{2+} + HPO_4^{2-} + OH^- + H_2O \quad (4.2)$$

$$HPO_4^{2-} + Ca(OH)_2 \rightarrow Ca^{2+} + PO_4^{3-} + OH^- + H_2O \quad (4.3)$$

$$5Ca^{2+} + 3HPO_4^{2-} + 4OH^- \rightarrow Ca_5(PO_4)_3OH(s) + 3H_2O \quad (4.4)$$

$$Ca_5(PO_4)_3OH(s) + F^- \rightarrow Ca_5(PO_4)_3F(s) + OH^- \quad (4.5)$$

$$5Ca^{2+} + 3PO_4^{3-} + F^- \rightarrow Ca_5(PO_4)_3F(s) \quad (4.6)$$

$$Ca^{2+} + F^- \rightarrow CaF_2\ (s) \quad (4.7)$$

We calculated grams needed for $NaH_2PO_4 \cdot H_2O$ and $Ca(OH)_2$ as 0.109 grams of $NaH_2PO_4 \cdot H_2O$ and 0.097 grams of $Ca(OH)_2$. We added these amounts of chemicals in 20 mL of 5 mg/L F^- and 100 mg/L F^-. The samples were shaken for an hour by the wrist shaker and resulting fluoride also measured after 3 days.

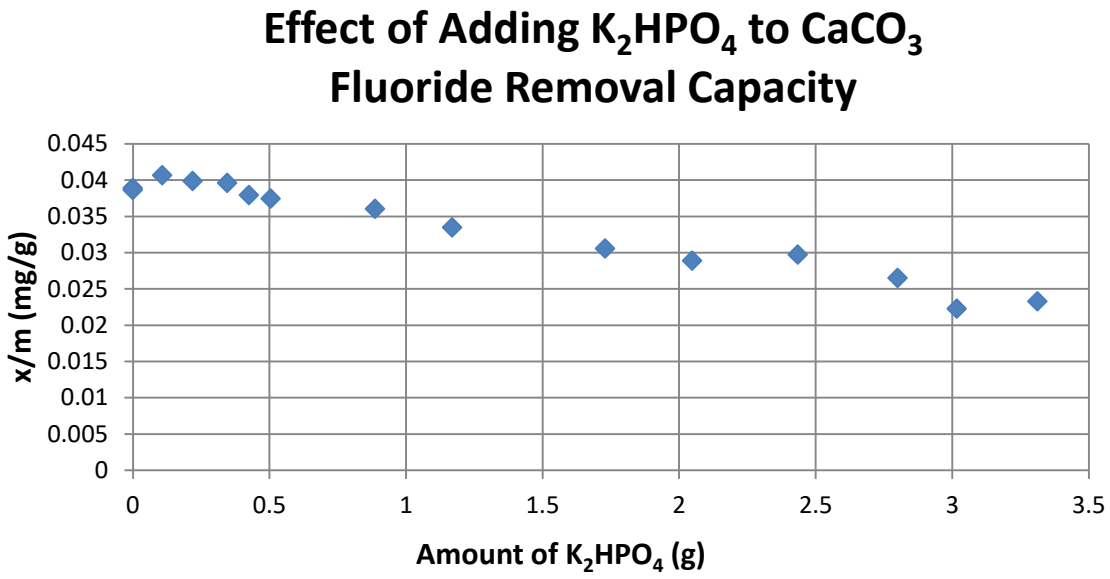

Fig. 4.1. Effect of adding K_2HPO_4 to calcium carbonate on fluoride removal capacity. As the amount of K_2HPO_4 increases, the fluoride removal capacity of $CaCO_3$ decreases. Amount of K_2HPO_4 (g) is plotted against x/m (mg/g).

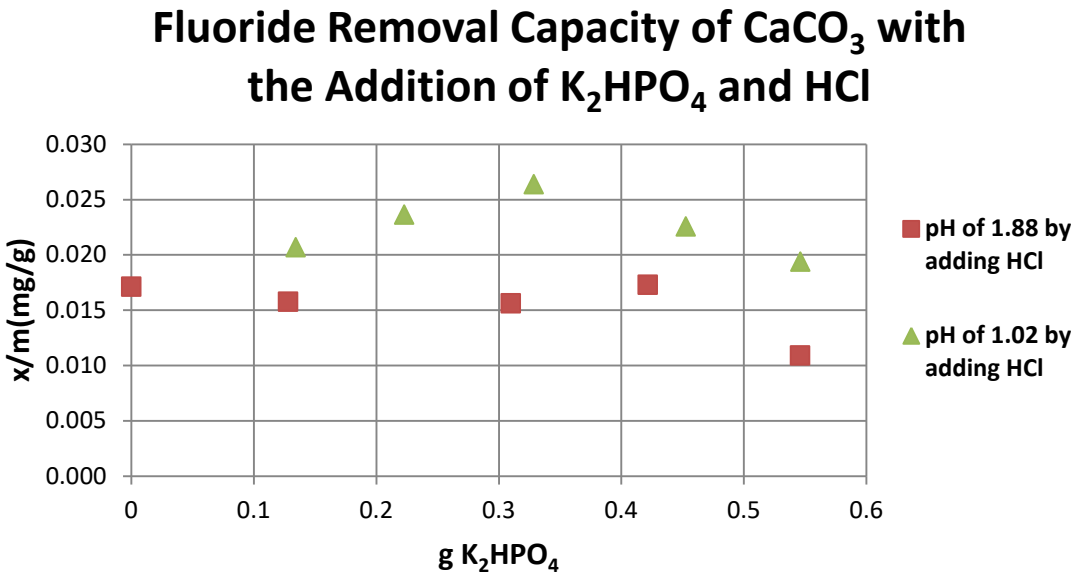

Fig. 4.2. Fluoride removal capacity of calcium carbonate with the addition of HCl and K_2HPO_4. Adding HCl to K_2HPO_4 and $CaCO_3$ does not improve fluoride removal capacity.

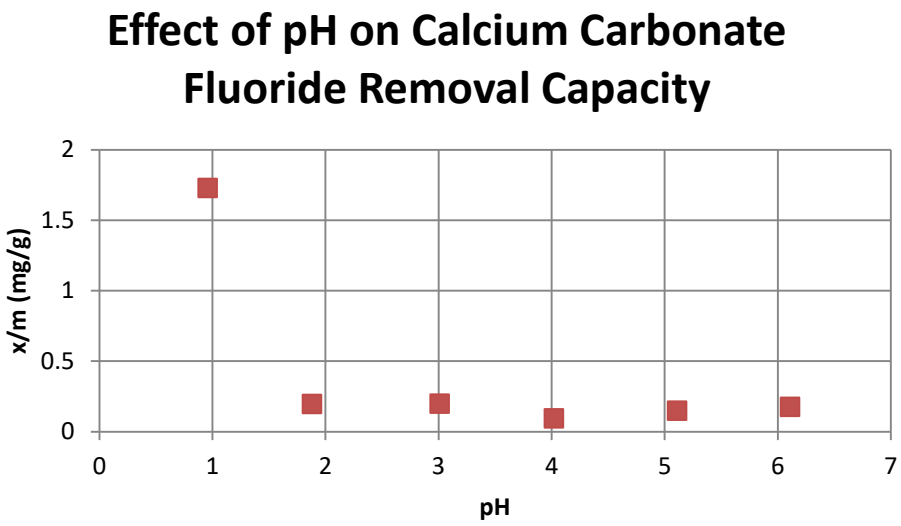

Fig. 4.3. Effect of pH on calcium carbonate fluoride removal capacity. Phosphoric Acid is added to the solution to lower pH. Adding phosphoric acid to the solution for a low pH less than approximately 1.5, improves fluoride removal capacity for calcium carbonate significantly.

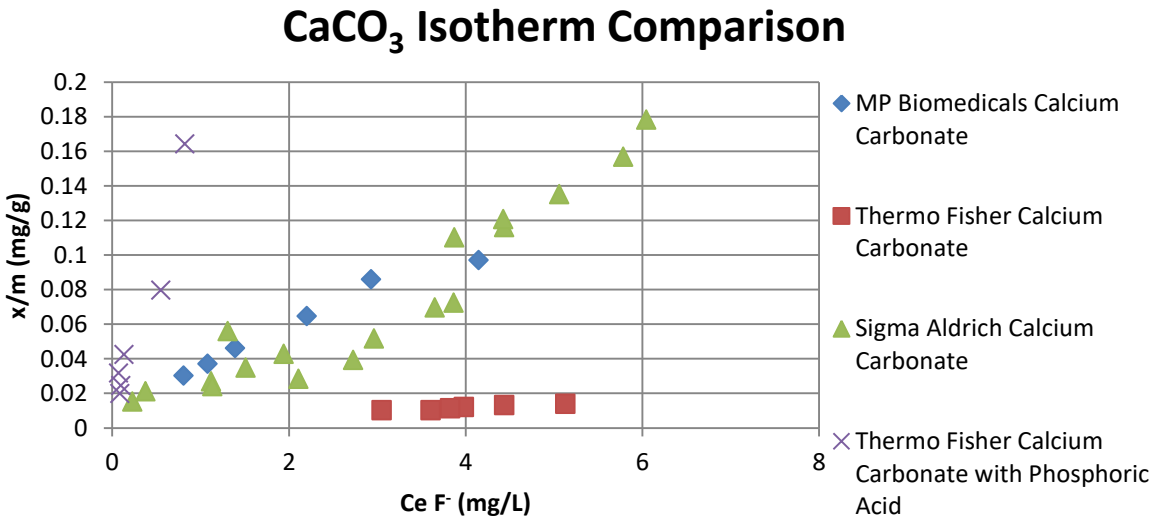

Fig. 4.4. Calcium carbonate isotherm comparison for different brands of calcium carbonate. When adding phosphoric acid to the brand with lowest adsorption capabilities, the fluoride removal is greatly increased.

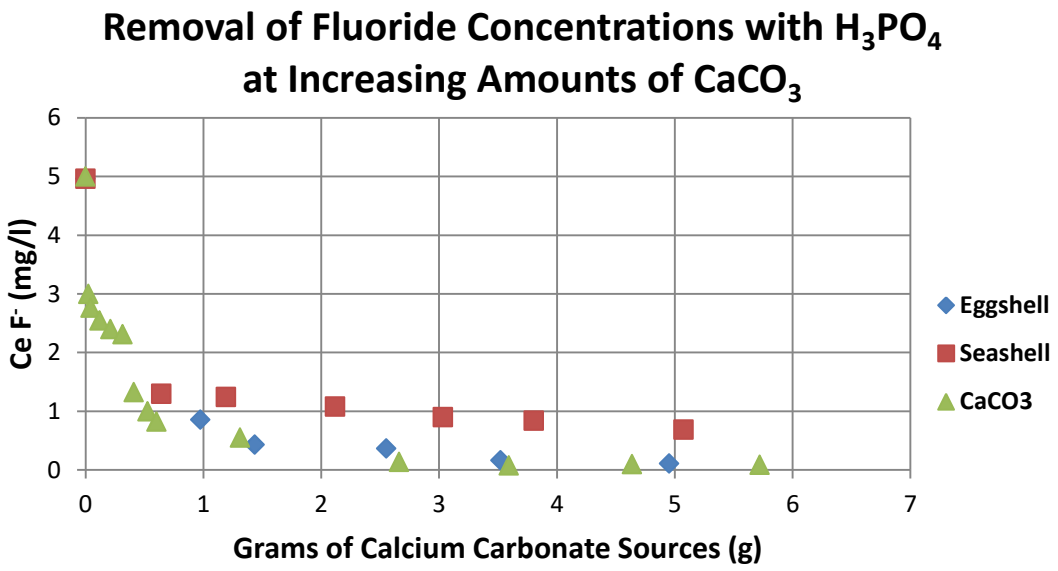

Fig. 4.5. Fluoride removal with H_3PO_4 and increasing amounts of calcium carbonate, eggshells and seashells. Fluoride concentrations went down to drinkable limits for all three, showing that any source of calcium carbonate with the presence of phosphoric acid will remove fluoride significantly.

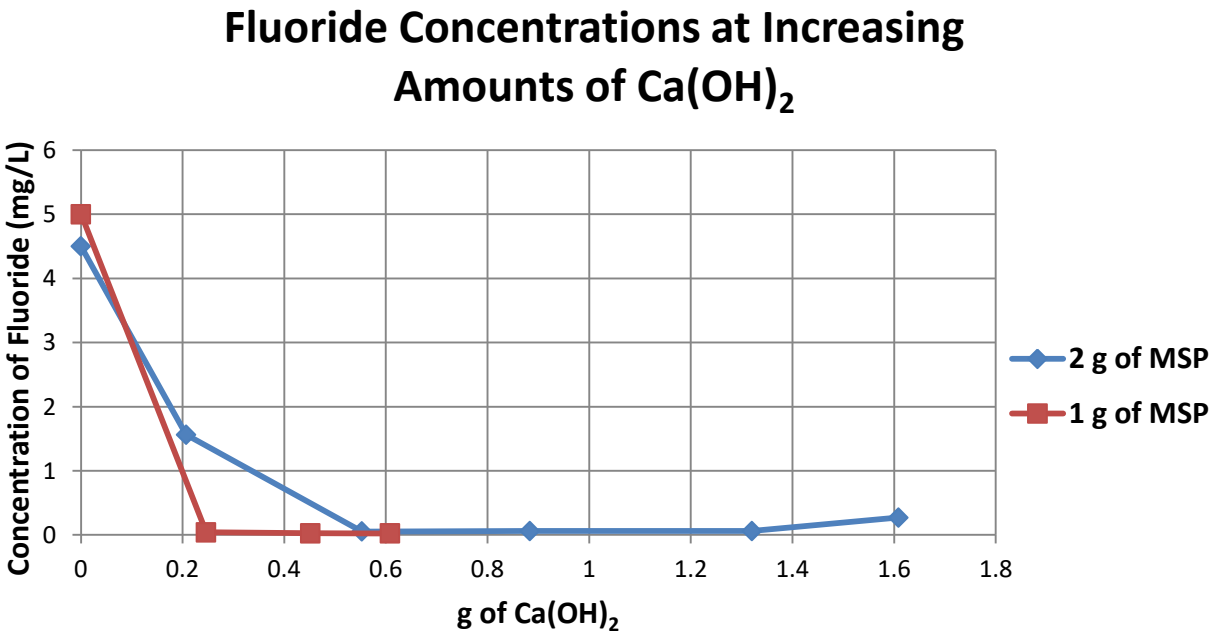

Fig 4.6. Concentration of fluoride at increasing amounts of $Ca(OH)_2$ with monosodium phosphate after 1 hr of shaking, showing near zero fluoride concentrations.

Table 4.1. Results of Defluoridation for Different Calcium Phosphate Systems using $Ca(OH)_2$, $CaCl_2$, H_3PO_4, NaH_2PO_4, and limestone rock

Calcium Phosphate Systems	**Methods**	**Comments**
$Ca(OH)_2$ with H_3PO_4 (pH_0 = 1)	increasing slaked lime (0.4-5 grams)	decreased fluoride concentrations down to 0.1 mg/L F^- till 3 grams or more ; after 3 grams, fluoride concentrations increased rapidly; a lot of precipitants were shown
$CaCl_2$ with H_3PO_4 (pH_0 =1)	increasing $CaCl_2$ (0.6-5.2 grams)	as amount of $CaCl_2$ increased, concentration of F- decreased down to 0.15 mg/L. pH decreased rapidly down to 0.
Limestone with H_3PO_4	Approximately 13 grams of limestone rock and increasing H_3PO_4(85% w/v) 0.6 mL- 1.17 mL	fluoride concentrations went down to 0.3 mg/L as amount of H_3PO_4 increased.
$Ca(OH)_2$ with NaH_2PO_4	2 grams of $Ca(OH)_2$ with increasing amounts of NaH_2PO_4 (0.46 g - 3 g)	As amount of NaH_2PO_4 increased, flouride concentrations decreased to 0.003 mg/L F^-. pH went from 13 down to 10.
$CaCl_2$ with NaH_2PO_4	2 grams of $CaCl_2$ with increasing amounts of NaH_2PO_4 (0.55 g-3.3 g)	As amount of NaH_2PO_4 increased, fluoride concentrations increased from 0.02 mg/L to 0.1 mg/L F^-, still well below drinking water limits. pH was very low ~ 2.

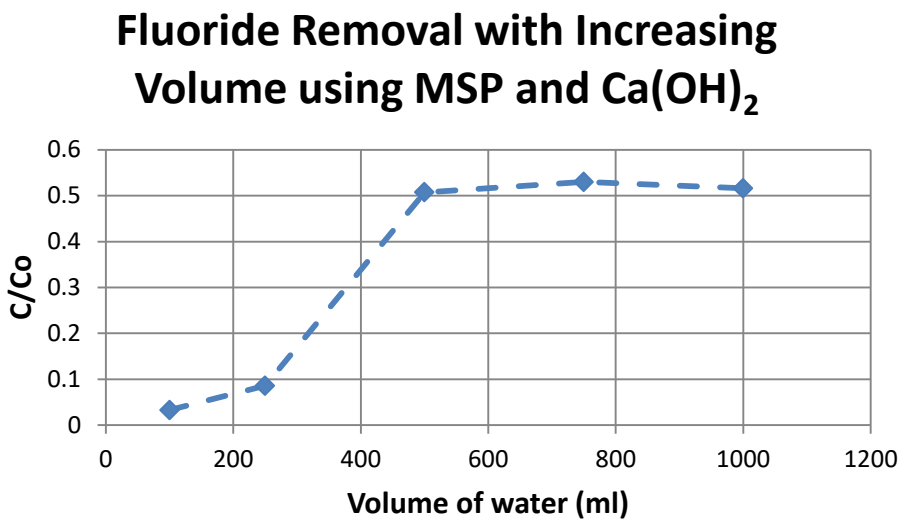

Fig. 4.7. Removal rate of fluoride using 0.45 g of $Ca(OH)_2$ and 1 g monosodium phosphate at increasing water volumes. Fluoride concentration at 1.5 mg/L at approximately 377 mL of water.

Table 4.2. Percentage of Fluoride Removed at Increasing Initial Fluoride Concentrations with 0.45 g $Ca(OH)_2$ and 1 g of monosodium phosphate

C_0 F- (mg/L)	C_e F- (mg/L)	% of Fluoride Removed
10	0.036	99.28
20	0.021	99.58
40	0.017	99.66
60	0.017	99.66
100	0.017	99.65

4.2 Results and Discussion

4.2.1 K_2HPO_4 Experiments

As we added increased amounts of K_2HPO_4 with $CaCO_3$, removal of $CaCO_3$ decreased from 0.04 mg/g to 0.023 mg/g. Adding KH_2PO_4 to $CaCO_3$ did not improve removal because the pH was too high (10.3 -10.4). There was not enough dissolution of $CaCO_3$ and concentration of Ca^{2+} to make $Ca_5(PO_4)_3OH(s)$ and CaF_2 precipitants. We tried to improve removal by adding HCl, but removal did not improve probably because the counter effect of adding K_2HPO_4 increased pH too much. 0.13 grams of K_2HPO_4 reduced the pH from 1.02 to pH of~6 rapidly (Figure 4.1; Figure 4.2)

4.2.2 $CaCO_3$ with Phosphoric Acid Experiments

Adding phosphoric acid to $CaCO_3$ increased removal dramatically. At 0.8 mg/L F^-, adsorption capacity went from 0.03 to 0.16, a 5.3 times increase. As the amount of phosphoric acid increased, calcium carbonate adsorption capacity increased. There needs to be a significant amount of phosphoric acid added because fluoride concentrations significantly decrease when pH is closer to 1, which is what Gogoi et al. (2015) used in his experiments (initial pH of 1.6). We saw that fluoride concentration decreased to 1.5 mg/L F^- at pH of 1.56 (Figure 4.3). We also determined that adding phosphoric acid to other forms of $CaCO_3$ (seashells and eggshells) improved fluoride removal. Using granular $CaCO_3$ and H_3PO_4 reduced fluoride concentrations from 5 mg/L to 0.01 mg/L; using eggshells and H_3PO_4 reduced fluoride concentrations to 0.02 mg/L; using seashells and H_3PO_4 reduced fluoride concentrations to as low as 0.7 mg/L (Figure 4.5).

Gogoi and Dutta (2016) explained the mechanism of the phosphoric acid and limestone system ($CaCO_3$) according to the following mechanisms:

$$CaCO_3(s) + 2H_3PO_4 \rightarrow Ca^{2+} + 2H_2PO_4^- + CO_2^- + H_2O \quad (4.8)$$

$$CaCO_3(s) + 2H_2PO_4^- \rightarrow Ca^{2+} + 2HPO_4^{2-} + CO_2^- + H_2O \quad (4.9)$$

$$Ca^{2+} + F^- \rightarrow CaF_2(s) \downarrow \quad (4.10)$$

$$5Ca^{2+} + 3HPO_4^{2-} + 4OH^- \rightarrow Ca_5(PO_4)_3OH(s) \downarrow + 3H_2O \quad (4.11)$$

$$Ca_5(PO_4)_3OH(s) + F^- \rightarrow Ca_5(PO_4)_3F(s) + OH^- \quad (4.12)$$

Dissolution of $CaCO_3$ is increased by adding phosphoric acid, increasing the amount of Ca^{2+} (Eq. 4.7; Eq. 4.8). Saturation of the solution occurs, and CaF_2 and calcium phosphate hydroxide (HAP) precipitants form (Eq. 4.9; Eq. 4.10). Fluoride also adsorbs to HAP to form fluorapatite (FAP) (Eq. 4.11). The sorption is an ion exchange physical adsorption and is a significant mechanism of removal in the phosphoric acid, calcium carbonate system (Gogoi and Dutta, 2016).

4.2.3 Different Calcium Phosphate Systems Experiments

We analyzed different calcium phosphate systems and found that for the $Ca(OH)_2$ and H_3PO_4 system, fluoride concentrations could be reduced from 5 mg/L to 0.1 mg/L. However, as amount of slaked lime increases, fluoride removal decreases because of the rapid increase of pH (~12.6). There is less dissociation of slaked lime, leading to less Ca^{2+} and HAP, CaF_2 and FAP precipitant formation. For the $CaCl_2$ and H_3PO_4 system, fluoride concentrations decreased to 0.15 mg/L, but the resulting pH was too low and not suitable for human consumption (~0). The pH decreased so rapidly probably due to the formation of HCl. The limestone with H_3PO_4

increased in fluoride removal capacity as phosphoric acid amounts increased. Fluoride concentrations decreased to 0.3 mg/L with approximately 13 grams of limestone, and the mechanisms are described in section 4.2.2. For the $CaCl_2$ and NaH_2PO_4 system, fluoride concentrations increased from 0.02 mg/L to 0.1 mg/L with increasing amounts of NaH_2PO_4, probably due to the formation of calcium hydrogen phosphate $CaHPO_4$ (solubility product $1 * 10^{-7}$ at 25 ^oC) or calcium phosphate ($2 * 10^{-29}$ at 25 ^oC). The proposed mechanism is below:

$$CaCl_2 + H_2PO_4^- = HCl + Cl^- + HPO_4^{2-} + Ca^{2+} \quad (4.13)$$

$$CaCl_2 + HPO_4^{2-} = PO_4^{3-} + Ca^{2+} + HCl + Cl^- \quad (4.14)$$

Even though fluoride concentrations were well below drinking water limits, this system would not be practical because pH is very low ~2 because of the formation of HCl. For the $Ca(OH)_2$ and NaH_2PO_4, we found the best results, with fluoride concentrations as low as 0.003 mg/L. The effectiveness is due to the fact that slaked lime easily dissociates in water as Ca^{2+} and can quickly form $Ca_5(PO_4)_3OH(s)$ because the solubility product of HAP is so low (~2.91×10^{-58} at 25 ºC). Additionally, adding NaH_2PO_4 will maintain pHs lower than say K_2HPO_4 because H_2PO_4 exists dominantly in the 2.12- 7.21 range, ensuring more dissociation of slaked lime and presence of Ca^{2+}. Fluorapatite also forms when fluoride adsorbs to HAP. Fluorapatite can also form when phosphate, fluoride and calcium ions precipitate (Eq. 4.5), but this would probably be more dominant in the pH range of > 12.35). The significant advantage of this system is that it uses no hazardous materials, such as concentrated acids (Table 4.1).

4.2.4 Slaked Lime $Ca(OH)_2$ and Monosodium Phosphate (NaH_2PO_4) Experiments

We found that fluoride concentration removal increased with the increase of NaH_2PO_4 (Table 4.1) and that adding increasing amounts of $Ca(OH)_2$ didn't help with increasing fluoride removal and at a certain point hindered fluoride removal (Figure 4.6). We added increasing amounts of slaked lime in Figure 4.6 (0.2-1.6 grams) with 2 grams of monosodium phosphate. 0.5 grams of slaked lime reduced fluoride concentrations down to 0.05 mg/L F^-. Adding more slaked lime didn't improve defluoridation but actually decreased defluoridation due to the rise in pH, causing less dissociation of ions and formation of HAP and FAP.

Experimentally, we found that when the amount of slaked lime to monosodium phosphate ratio was around 0.45, the solution would be at a neutral pH of approximately 7. We found that with these amounts of chemicals, initial fluoride concentrations up to 100 mg/L or more could be reduced to near zero concentrations (~0.02 mg/L F^-), and that a volume of approximately 337 mL of water could be treated when initial fluoride concentration is ~ 5 mg/L. (Figure 4.7; Table 4.2). For a single person to drink 2 liters of defluoridated water a day, it would take 5.93 grams of monosodium phosphate and 2.67 grams of slaked lime. For a family of four to drink 8 liters of defluoridated water a day, it would take 23.72 grams of monosodium phosphate and 10.68 grams of slaked lime.

It is not possible to generally predict costs because the cost of the chemicals varies by location. However, a rough estimate can be calculated. Fawell et al. (2006) gave an estimate of $0.86/ kg of monosodium phosphate and $0.06/ kg of lime. For a single person to drink 2 liters of defluoridated a day, it would cost roughly US$ 0.005 for MSP and US$ 0.00016 for lime. For

a family of four to drink 8 liters of defluoridated water a day, it would cost roughly US$ 0.02 for MSP and US$ 0.00064 for lime (Fawell et al., 2006, COWI, 1998).

We also stoichimetrically calculated how much one would need to remove all the F^- using equations 4.1-4.5. To remove 5 mg of fluoride, we would need 0.109 grams of $NaH_2PO_4 \cdot H_2O$ and 0.097 grams of $Ca(OH)_2$. Below are the calculations:

$$\frac{(5\ mgF^-)}{19\frac{mg}{mmol}F^-} * \frac{1\ mmol\ HAP}{1\ mmol\ F^-} * \frac{3\ mmol\ {PO_4}^{3-}}{1\ mmol\ HAP} * \frac{1 mmol\ MSP}{1\ mmol\ {PO_4}^{3-}} * \frac{138\ mg\ MSP}{1\ mmol\ MSP}$$

$$= 109\ mg\ MSP$$

$$\frac{(5\ mg\ F^-)}{19\frac{mg}{mmol}F^-} * \frac{1\ mmol\ HAP}{1\ mmol\ F^-} * \frac{5\ mmol\ Ca^{2+}}{1\ mmol\ HAP} * \frac{1 mmol\ Ca(OH)_2}{1\ mmol\ Ca^{2+}} * \frac{74\ mg\ Ca(OH)_2}{1\ mmol\ Ca(OH)_2}$$

$$= 97\ mg\ Ca(OH)_2$$

To test the stoichiometry, we performed an experiment in stoichiometric ratios at 100 mg/L initial F^- concentration. The fluoride concentration decreased to 17 mg/L after one hour. A similar experiment at 5 mg/L F^- initial concentration reduced to 3.5 mg/L F^- after one hour and ~ 3.2 mg/L F^- after three days. The experiment was continued for three days to ensure that an equilibrium existed. The stoichiometric amounts did not completely remove all the fluoride probably because other reactions consumed PO_4^- , such as calcium phosphate.

4.3 pH Calculations

To verify the pH results we obtained empirically, we did chemistry pH calculations. To show that 0.78 mL of phosphoric acid (85% w/v) does decrease the solution down to a pH ~ 1, we looked at different chemistry equations (Butler, 1998) :

$Ka_{1=}\frac{[H^+][H_2PO4^-]}{[H_3PO_4]}$; $Ka_1 = 7.5 * 10^{-3}$

$Ka_{2=}\frac{[H^+][HPO4^{2-}]}{[H_2PO4^-]}$; $Ka_2 = 6.2 * 10^{-8}$

$Ka_{3=}\frac{[H^+][PO4^{3-}]}{[HPO4^{2-}]}$; $Ka_3 = 5.8 * 10^{-13}$

$C= [H_3PO_4] + [H_2PO4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$

Calculation of C for phosphoric acid:

$1.685\ g/ml * 0.78\ ml = 1.314\ g$

$$\frac{1.314\ g}{20.78\ ml} = \frac{0.0632\ g}{ml}$$

$$\frac{0.0632\ g}{ml}\ H_3PO_4 * \frac{1 mol\ H_3PO_4}{98\ g\ H_3PO_4} = 0.645\ M$$

"Fraction of acid present as each species is the ratio of the concentration of that species to the analytical concentration C" (Butler, 1998):

$$\alpha_2 = \frac{[H_2PO4^-]}{C}$$

$$\frac{1}{\alpha_2} = \frac{C}{[H_2PO4^-]}$$

$$\frac{1}{\alpha_2} = \frac{[H_3PO_4] + [H_2PO4^-] + [HPO4^{2-}] + [PO4^{3-}]}{[H_2PO4^-]}$$

Substitute with Ka values

$$\frac{1}{\alpha_2} = \frac{[H^+]}{Ka_1} + 1 + \frac{Ka_2}{[H^+]} + \frac{Ka_2Ka_3}{[H^+]^2}$$

$$\frac{1}{\alpha_2} = \frac{[H^+]^3}{Ka_1[H^+]^2} + \frac{Ka_1[H^+]^2}{Ka_1[H^+]^2} + \frac{Ka_1Ka_2[H^+]}{Ka_1[H^+]^2} + \frac{Ka_1Ka_2Ka_3}{Ka_1[H^+]^2}$$

$$\alpha_2 = \frac{Ka_1[H^+]^2}{[H^+]^3 + Ka_1[H^+]^2 + Ka_1Ka_2[H^+] + Ka_1Ka_2Ka_3}$$

Last two terms in denominator are negligible

Proton condition :

$[H^+] = [H_2PO4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [OH^-]$

$[H_2PO4^-]$ is significantly greater than $[HPO_4^{2-}] + [PO_4^{3-}] + [OH^-]$ at pH of 2.23-7.21

$[H^+] = [H_2PO4^-]$

$[H^+] = C\ \alpha_2$

$[H^+] = C * \frac{Ka_1[H^+]^2}{[H^+]^3 + Ka_1[H^+]^2}$

$CK_{a1} = [H^+]^2 + Ka_1[H^+]$

$0 = [H^+]^2 + Ka_1[H^+] - CK_{a1}$

use the quadratic formula

$$[H^+] = \frac{\left(-K_{a1} + \sqrt{K_{a1}{}^2 + 4CK_{a1}}\right)}{2}$$

$[H^+] = 0.066$ M

pH~ 1.18

We wanted to verify that 4.015 grams of $CaCO_3$ gave us a pH of ~ 4.7 when combined with 0.78 mL of phosphoric acid (85% w/v), which we found empirically.

$$CaCO_3\ M = \frac{4.0152\ grams * \frac{1\ mole\ of\ CaCO_3}{100\ g\ of\ CaCO_3}}{20.78\ ml * \frac{1l}{1000\ ml}} = 1.93\ M$$

0.066 M of H^+ reacts with $CaCO_3$ to form 0.066 M of HCO_3^- and 1.864 moles of H_2CO_3

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = K_{a1} = 10^{-6.3}$$

$[H^+] = 1.41 * 10^{-5}$

pH= -log $[H^+]$~ 4.84 , which is close to 4.7

We also verified that 0.45 g of $Ca(OH)_2$ and 1 g of NaH_2PO_4 gives us around a neutral pH (Loberg and Yee, 2016):

H_2PO4^- = $\frac{1g}{97\frac{g}{mol}}$ =0.01 moles of H_2PO4^-

$Ca(OH)_2$ = $\frac{0.45\ g}{74\frac{g}{mol}}$= 0.006 moles of $Ca(OH)_2$

$Ca(OH)_2$ and H_2PO4^- react to form 0.006 moles of HPO_4^{2-} and 0.004 moles of H_2PO4^- remain

$Ka_2 = \frac{[H^+][HPO4^{2-}]}{[H_2PO4^-]}$

$Ka_2 = 6.2 * 10^{-8} = \frac{[H^+][0.006\ \text{moles}]}{[0.004\ moles]}$

pH= - log $[H^+]$ = ~ 7.37

4.4 Conclusion

Because calcium carbonate adsorption did not have high adsorption capacities from previous experiments, new experiments were performed to find ways to improve fluoride removal rates. Different calcium phosphate systems were analyzed and results explained. K_2HPO_4 would not be a good option because the increase of pH hinders defluoridation. HPO_4 exists dominantly in the 7.21- 12.32 pH range. $CaCl_2$ would not be a good option because it decreases pH to undrinkable levels due to the formation of HCl. Adding phosphoric acid and calcium carbonate were effective in increasing fluoride removal rates. Adding phosphoric acid increased calcium carbonate adsorption capacity by 5 times. However, there would need to be a significant amount of phosphoric acid and initial pH would need to be really low to have optimal removal rates (pH ~1.5 or less). We found the best results by using $Ca(OH)_2$ and $NaH_2PO_4$with fluoride concentrations decreasing to 0.003 mg/L F^-. The effectiveness is due to the fact that slaked lime easily dissociates in water as Ca^{2+} and can quickly form $Ca_5(PO_4)_3OH(s)$ because of

the low solubility product of HAP. Fluoride is removed when fluoride adsorbs to HAP and forms FAP. Additionally, adding NaH_2PO_4 will keep pHs low enough because H_2PO_4 exists dominantly in the 2.12- 7.21 range. A neutral pH could be attained when the ratio of the amount of slaked lime to the amount of monosodium phosphate was ~ 0.45.

For a single person to drink 2 liters of defluoridated water a day from an initial concentration of 5 mg/L, it would take approximately 5.93 grams of monosodium phosphate and 2.67 grams of slaked lime. For a family of four to drink 8 liters of defluoridated water a day, it would take approximately 23.72 grams of monosodium phosphate and 10.68 grams of slaked lime. The significant advantage of this system is that it uses no hazardous materials, such as acids. Further studies include finding minerals that naturally contain monosodium phosphate, determining if this slaked lime, monosodium phosphate system will also treat other contaminants, like arsenic and radionuclides, and assembling a household sized defluoridation unit.

5. CONCLUSION

Approximately one ninth of the world's population does not have access to a safe drinking water source. One fourth of the population in developing countries live under acute water shortage and the water that is available can be contaminated with fecal matter and other physical, biological, radiological, and chemical contaminants. One specific contaminant of concern is excessive fluoride in water. Water with concentrations of 1.5 mg/L F^- or lower strengthens our bones and teeth, but above this concentration, there are many detrimental effects, ranging from "mottled teeth" and tooth decay in the 1.5 -4 mg/L F^- to stooped backs and crooked hands and feet in the 4 mg/L – 10 mg/L F^- range. Many countries around the world are affected by excessive fluoride in water, such as China, India, Sri Lanka, Pakistan, and the Rift Valley countries in Africa. Our water can be contaminated with excessive fluoride through anthropogentic industrial process, such as cement and brick manufacturing, electronics and steel manufacturing, and aluminum and iron smelting. Large geographical belts are also affected with fluoride in water due to volcanic activity and sediments from mountains that have marine origins. Another large source of fluoride contamination is fluoride-containing minerals and rocks that come into contact with groundwater (Gupta and Ayoob, 2016; UNICEF and WHO, 2012; WHO, 2016; EPA, 2016; Fawell et al., 2006; Nath and Dutta, 2010).

In developing countries, where resources are limited, it is important to allocate resources appropriately to the most essential problems first. In locations where fluoride concentrations in drinking water are excessive but only cause negative aesthetic consequences, such as mottled teeth, it may not be as essential to allocate funds to the area first. However, at higher concentrations of fluoride, around the 4- 10 mg/L F^-, where skeletal fluorosis leading to crippling

fluorosis occurs, it is essential to allocate funds to this problem. Excessive fluoride in water negatively affects a person's basic ability to function, and has negative neurological affects, causing serious economic and social consequences to the government and the people. People are forced to retire early from working and depend on others, and children are immobile to do basic daily tasks (Datturi et al., 2015; Ayoob and Gupta, 2016). An example of a country heavily affected by excessive fluoride in water is India. In an Indian governmental document by the Water and Sanitation Program and the Ministry of Rural Development Department of Drinking Water and Sanitation, it stated that drinking water quality in rural areas is a "key policy concern for the Government of India." Other than bacteriological contamination due to poor sanitation, fluoride is one of the top contaminants of concern along with arsenic (Kullapa, 2011).

However, developing countries often do not have the means for technologically-advanced and expensive technology to treat contaminants in water. Some processes that would treat excessive fluoride in water are coagulation, adsorption, electrochemical methods, and membrane processes. Adsorption and precipitation are the processes most commonly used in developing countries since electrochemical methods and membrane processes are expensive and usually require some type of imported technology. Some common adsorbents used are activated alumina, clay, limestone powder, "bone charcoal." Some common precipitation chemicals include lime, calcium, magnesium salts, and alum (Ayoob and Gupta, 2008; Dutta et al., 2016). All of these methods have their advantages and disadvantages.

Developing countries also do not always have the means to have centralized water treatment systems. Therefore, an onsite defluoridation treatment system is needed that requires no special operational expertise, does not use hazardous chemicals, and is sustainable by the

local people. In this dissertation, we have studied using calcium carbonate as an adsorbent to use in an onsite treatment system. In our calcium carbonate adsorption studies, we determined that calcium carbonate is able to decrease fluoride concentrations down to drinkable water limits via physical adsorption. The advantage of this system is that calcium carbonate can be found in abundant quantities naturally around the world. However, the significant disadvantage is the large amount of calcium carbonate needed. Our unoptimized treatment system will require approximately 1.67 kg of calcium carbonate per day to defluoridate 2 liters of water with an initial concentration of 7 mg/L F^-. Renewal and regeneration by simple scrubbing or using this system for lower fluoride quantities (~ 5 mg/L F^- or lower) would lower the amount of $CaCO_3$ needed, as well as lowering pH or reducing particle size of the adsorbent.

We also studied ways to improve the calcium carbonate treatment system by adding phosphate materials. We studied different combinations of calcium and phosphate materials: $CaCO_3$, $CaCl_2$, $Ca(OH)_2$, H_3PO_4, KH_2PO_4, $NaHPO_4$. We found that by adding phosphoric acid to calcium carbonate, removal of fluoride improved by 5.3 times (Gogoi et al., 2015). The disadvantage of this system is the use of phosphoric acid that could be dangerous for the people to use. The most effective calcium phosphate system we found was the monosodium phosphate (NaH_2PO_4) and calcium hydroxide system ($Ca(OH)_2$) system, which reduced fluoride concentrations to 0.003 mg/L. 5.93 grams of monosodium phosphate and 2.67 grams of slaked lime could defluoridate water from an initial concentration of 5 mg/L. Further studies should include performing a pilot study and making a household treatment system using NaH_2PO_4 and $Ca(OH)_2$, finding minerals that naturally contain phosphate, and testing if a phosphate-containing mineral and slaked lime system can also treat other contaminants, such as arsenic and

radionuclides. We are hopeful that this monosodium phosphate, slaked lime system can be used as an onsite defluoridation system that can bring fluoride safe water to more people.

REFERENCES

Abdel-Jabbar, N. and Al-asheh, S. 2009. Factorial design for the analysis of packed bed sorption of copper using eggshell as a biosorbent, J. Environ. Protec. Sci. 22, 3133- 139.

Adler, H., Klein, G. 1938. Removal of fluorides from potable water by tricalcium phosphate. Indus. Eng. Chem. 30 (2), 163-165.

Adler, P. , Armstrong, W.D., Bell, M., Bhurssry, B.R., Buttner,W., Cremer, H., Demole, V., Ericsson, Y., Gedalia, I., Hodge, H., Jenkins, G., Jolly, S., Largent, E., Leone, N., Ludwig, T., Martin, A., Minoguchi, G., Muhler, J., Schlesinger, E., Siddiqui, A., Singer, L., Singh, A., Smith, F., Stookey, G., Taves, D., Venkateswarlu, P., Weatherell, J., Weidmann, S., Zipkin, I. 1970. Fluorides and human health. World Health Organization Monograph Series No. 59. Geneva, Switzerland.

Aldrees, A.M. and Al-Manea, S.M. 2010. Fluoride content of bottled drinking waters available in Riyadh, Saudi Arabia, Saudi Dent. J. 22, 189-93.

Amalraj, A. and Pius, A. 2013. Health risk from fluoride exposure of a population in selected areas of Tamil Nadu South India, Food Sci. Hum. Wellness. 2, 75, 86.

Amini, M., Mueller, K., Abbaspour,K., Rosenberg, T., Afyuni, M., Moller, K., Sarr, M., Johnson, A. 2008. Statistical modeling of global geogenic fluoride contamination in groundwaters. Environ. Sci. Technol. 42, 3662-3668.

Arnold, F., Dean, H., Jay, P., Knutson, J. 1956. Effect of fluoridated public water supplies on dental caries prevalence. 10th year of the Grand Rapids Muskegon study. Public Health Rep. 71, 652-658.

Asgari, G., Roshani, B., Ghanizadeh, G. 2012. The investigation of kinetic and isotherm of fluoride adsorption onto functionalize pumice stone. J. Hazard. Mater. 217-218, 123-132.

ASTDR. 2013. Report on toxicological profile for fluorides, hydrogen fluoride and fluorine. U.S. Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry: Atlanta, GA. astdr

Aravind, A., Dhanya, R., Narayan, A., Sam, G., Adarsh, V., Kiran, M. 2016. Effect of fluoridated water on intelligence in 10-12-year-old school children. J. Int. Soc. Prev. Community Dent. 6(3), S237-S242.

Ayoob, S. and Gupta, A.K. 2006. Fluoride in drinking water: a review on the status of stress effects, Crit. Rev. Environ. Sci. Technol. 36, 433-487.

Ayoob, S., Gupta, A.K. and Bhat, V.T. 2008. A conceptual overview on sustainable technologies for the defluoridation on drinking water, Crit. Rev. Environ Sci. Technol. 38, 401-470.

Barnum, D. 1999. Predicting acid-base titration curves without calculations. J. Chem. Edu. 76 (7), 938.

Bell, L., Mika, H., Kruger, B. Synthetic hydroxyapatite- solubility product and stoichiometry of dissolution.1978. Archs Oral. Biol.23, 329-336.

Bell, M., Largeut, E., Ludwig, T., Muhler, J., Stookey, G. 1970. Fluorides and human health. WHO Monograph Series No. 59: Geneva, Switzerland.

Ben Nasr, A.,Walha, K., Charcosset, C., Ben Amar, R. 2011. Removal of fluoride ions using cuttlefish bones, J. Fluorine Chem. 132, 57–62.

Bengharez, Z., Farch, S., Bendahmane, M., Merine, H. and Benyahia, M. 2012. Evaluation of fluoride bottled water and its incidence in fluoride endemic and non-endemic areas, SPEN. J., 7, 41-45.

Bhargava, D., Killedar, D. 1991. Batch studies of water defluoridation using fishbone charcoal, J. Water Pollut. Control Fed. 63, 848–858.

Bhatnagar, A., Kumar, E., Sillanpaa, M. 2011. Fluoride removal from water by adsorption-a review. Chem. Eng. J. 171, 811-840.

Bhatt, P., Paul, P., 2008. Analysis of urinary stone constituents using powder X-ray diffraction and FT-IR. J. Chem. Sci. 120, 267-273.

Bhaumik, R., Mondal, N.K., Das, B., Roy, P., Pal, K.C., Das, C. 2012. Eggshell powder as an adsorbent for removal of fluoride from aqueous solution: equilibrium, kinetic and thermodynamic studies. E. J. Chem. 9 (3), 1457-1480.

Bi, H., Xiong, Y., Yi, W. 1993. Experimental study on removal of fluoride. Xi'an Medical University.Wat. Cal. Phos. J. 14(1), 90-92.

Biswas, K., Gupta, K., Ghosh, U. 2009. Adsorption of fluoride by hydrous iron(III)- tin(IV) bimetal mixed oxide from the aqueous solutions. J. Chem. Eng.149, 196-206.

Bower, C., Hatcher, J. 1967. Adsorption of fluoride by soils and minerals. Soil Sci. 103(3), 151-154.

Broeck, K., Hoornick, N., Hoeymissen, J., de Boer, R., Giesen, A., Wilms, D. 2003. Sustainable treatment of HF wastewaters from semiconductor industry with a fluidized bed reactor. IEEE Trans. Semicond. Manuf. 16, 423–428.

Bulusu, K., Nawlakhe, W., Patil, A., Karthikeyan, G. 1993. Water quality and defluoridation techniques and their limitations. Prevention and Control of Fluorosis, Rajiv Gandhi National Drinking Water Mission: New Delhi, India, 11.

Bulusu, K.R. 1984. Defluoridation of water using combination of aluminum chloride and aluminum sulfate. J. Inst. Eng. 65, 22-26.

Butler, J. 1998. Ionic equilibrium solubility and pH calculations. New York, NewYork: John Wiley & Sons, Inc.

Buzalaf, M.A., de Almeida, B.S., Cardoso, V.E., Olympio, K.P. and Furlanj, T. de A. 2004. Total and acid-soluble fluoride content of infant cereals, beverages and biscuits from Brazil, Food Addit. Contam., 21, 210-5.

Calderon, J., Blenda, M., Marielena, N., Leticia, C., Deogracias, O.M., Diaz-Barriga, F. 2000. Influence of fluoride exposure on reaction time and visuospatial organization in children, Epidemiology. 11, 153.

Camargo, J. 2003. Fluoride toxicity to aquatic organisms: a review, Chemosphere. 50, 251-264.

Carton, R. 2006. Review of the 2006 United States National Research Council report: fluoride in drinking water. Guest Edit. Rev. Fluoride. 39(3), 163-172.

Castel, C., Schweizer, M., Simonnot, M.O. and Sardin, M. 2000. Selective removal of fluoride ions by a two-way ion-exchange cyclic process, Chen. Eng. Sci. 55, 3341-3352.

CDC. 2014. Private water systems. CDC: Atlanta, Georgia. https://www.cdc.gov/healthywater/drinking/private/index.html

CDC. 2014. Water-related diseases and contaminants in public water systems. CDC: Atlanta, Georgia. https://www.cdc.gov/healthywater/drinking/public/water_diseases.html

CDC. 2015. Water treatment. CDC: Atlanta, Georgia. https://www.cdc.gov/ healthywater/drinking/public/ water_treatment.html

Chandrajith, R., Dissanayake, C.B., Ariyarathna, T., Herath, H.M. and Padmasiri, J.P. 2011. Dose-dependent Na and Ca in fluoride-rich drinking water-another major cause of chronic renal failure in tropical arid regions, Sci. Total Environ. 409, 671-675.

Chauhan, V.S., Dwivedi, P.K., Iyengar, L. 2007. Investigations on activated alumina based on domestic defluoridation units, J. Hazard. Mater., 139, 103-107.

Choi, W.W. and Chen, K.Y. 1979. The removal of fluoride from waters by adsorption, J. AWWA. 71, 562-570.

Christoffersen, M., Christoffersen, J., Arends, J. 1984. Kinetics of dissolution of calcium hydroxyapatite:VII. The effect of fluoride ions, J. Cryst. Growth. 67, 107–114.

Clesceri, L., Greenberg, A. 1998. Standard methods for the examination of water and wastewater eaton AD, 20th ed. APHA, AWWA, WEF: Washington, DC, 4- 82.

COWI. 1998. Review of practical experiences with defluoridation in rural water supply programmes part II. Ministry of Foreign Affairs: Danida, Copenhagen, 73.

Crittenden, J., Trussell, R., Hand, D., Howe, K., Tchobanoglous, G. 2012. MWH Water Treatment Principles and Design 3rd ed. John Wiley and Sons, Inc.: Hoboken, New Jersey.

Dahi, E. 1996. Contact precipitation of defluoridation of water. 22nd WEDC Conference, New Delhi, India, 9-13.

Dahi, E., Bregnhøj, H., Orio, L. 1997. Sorption Isotherms of fluoride on flocculated alumina. The Proceedings of the First International Workshop on Fluorosis and Defluoridation of Water. Tanzania, Africa, 18-22.

Dahi, E., Mtalo, F., Njau, B. and Bregnhj, H. 1996. Defluroidation using the Nalgonda technique in Tanzania. In: 22nd WEDC Conference, Reaching the Unreached: Challenges for the 21st Century, New Delhi, India, 266-268.

Dahi, E., Nielsen, J. 1997. Proceedings of the 2nd International Workshop on Fluorosis Prevention and Defluoridation of Water : Nazareth, Ethiopia.

Dahi, E.1998. Small community plants for low cost defluoridation of water by contact precipitation. Proceedings of the 2nd International Workshop on Fluorosis and Defluoridation of Water. Nazareth, 19-22.

Das, B., Hazarika, P., Saikia, G., Kalita, H., Goswami, D., Das, H., Dube, S., Dutta, R., 2007. Removal of iron from groundwater by ash, a systematic study of a traditional method. J. Hazard. Mater. 141, 834-841.

Datturi, S., Steenbergen, F., Beusekom, M., Kebede, S. 2015. Comparing defluoridation and safe sourcing for fluorosis mitigation in the Ethiopian Central Rift Valley. Fluoride. 48(4), 293-314.

Daw, R.K. 2004. Experiences with domestic defluoridation in India. Proceedings of the 30th WEDC International Conference on people-centered approaches to water and environmental sanitation : Vientiane, Lao PDR. 467-473.

Dawson, B.J.M., and Belitz, Kenneth, 2012, Status of groundwater quality in the California Desert Region, 2006–2008—California GAMA Priority Basin Project: U.S. Geological Survey Scientific Investigations Report 2012–5040, 110.

Dean, H. 1993. Distribution of mottled enamel in the United States. Public Health Rep. 48(25), 703-734.

Devi, R., Alemayehu, E., Singh, V., Kumar, A., Mengistie, E. 2009. Removal of fluoride, arsenic and coliform bacteria by modified homemade filter media from drinking water. Biosource Tech. 99, 2269-2274.

Dinesh, C. 1998. Fluoride and human health cause for concern. Ind. J. Environ. Protec. 19(2), 81-89.

Du, L., Wan, C., Cao, X. and Liu, J. 1992. The effect of fluorine on the developing human brain, Chin. J. Pathol. 21, 218-220.

Dutta, R., Gogoi, S., Borah, A., Mohan, R., Nath, S. 2016. Field trial of fluoride removal by phosphoric acid-crushed limestone treatment. Proceedings of the 13th IWA Specialized Conference on Small Water and Wastewater Systems: Athens, Greece.

Dutta, R., Saikia, G., Das, B., Bezbaruah, C., Das, H., Dube, S. 2006. Fluoride contamination in groundwater of Central Assam, India. Asian J. of Water Environ. and Pollut. 3, 93-100.

Ebbing, D., Gammon, S. 2009. General Chemistry 9th ed. Houghton Mifflin Company: Boston, Massachusetts.

EPA. 2016. Contaminant candidate list and regulatory determination, types of drinking water contaminants. Environmental Protection Agency: Washington, District of Columbia. https://www.epa.gov/ccl/types-drinking-water-contaminants.

Fan, X., Parker, D., Smith, M. 2003. Adsorption kinetics of fluoride on low cost materials, Water Res. 37, 4929–4937.

Fawell, J., Bailey, K., Chilton, J., Dahi, E., Fewtrell, L., Magra, Y. 2006. Flouride in Drinking Water. IWA and WHO: London, UK.

Freundlich, H. 1906. Over the adsorption in solution. Z. Phys. Chem. 57(A), 385.

Gadgil, A. 1998. Drinking water in developing countries. A. Rev. E. and Environ. 23, 253-286.

Garcia, M., Borgnino, L., 2015. Fluoride in the context of the environment. Food and Nutritional Components in Focus No. 6. Royal Society of Chemistry: London, England.

Ghorai, S. and Pant, K. 2005. Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina. Sep. Pur. Technol. 42, 265-271.

Gogoi, S. and Dutta, R. 2016. Mechanism of fluoride removal by phosphoric acid-enhanced limestone equilibrium and kinetics of fluoride sorption. Desal. Water Treat. 57, 6838-6851.

Gogoi, S., Dutta, R. 2016. Fluoride removal by hydrothermally modified limestone powder using phosphoric acid. J. Environ. Chem. Eng. 4, 1040-1049.

Gogoi, S., Nath, S., Bordoloi, S., Dutta, R. 2015. Fluoride removal from groundwater by limestone treatment in presence of phosphoric acid. J. Environ. Manag. 152, 132-139.

Gupta, A.K., Ayoob, S. 2016. Fluoride in drinking water: status, issues, and solutions. CRC Press: Boca Raton, Florida.

Gupta, S.K., Gupta, A.B., Dhindsa, S.S., Seth, A.K., Agrawal, K.C. and Gupta, R.C. 1999. Performance of domestic filter based on KRASS defluoridation process. J. Indian Water Works Assoc. 31, 193-200.

Hamann, S. 1970. Titration behavior of monoprotic and diprotic acids. J. Chem. Edu. 47 (9), 658.

Handa, B. 1975. Geochemistry and genesis of fluoride-containing ground waters in India, Groundwater. 13(3).

Hao, J., Huang, C.1986. Adsorption characteristics of fluoride onto hydrous alumina. J. Environ. Eng. ASCE. 112, 1054-1067.

He, G., and S. Cao. 1996. Assessment of fluoride removal from drinking water by calcium phosphate systems, Int. Soc. for FIuor. Research. 29 (4), 212-216.

He, G., Ji, R., Zhang Y. 1995. Mechanisms of defluoridation of drinking water by tricalcium phosphate. Proceedings of the 1st International Workshop on Fluorosis and Defluoridation of Water: Ngurdoto, Tanzania.

Heilman, J.R., Kiritsy, M.C., Levy, S.M. and Wefel, J.S. 1999. Assessing fluoride levels of carbonated soft drinks, J.Am. Dent. Assoc. 130, 1593-1599.

Heilman, J.R., Kiritsy, M.G., Levy, S.M. and Wefel, J.S. 1997. Fluoride concentrations of infant foods, J. Am. Dent. Assoc. 128, 857-863.

Heman, L., Srivastava, R., Sinhua, A. 2002. A precise U-Pb zircon/baddeleyite age for the jasra igneous complex, Karbi-Analog, District, Assam, NE, India. Curr. Sci. 82, 744.

Hill, J., Petrucci, R., McCreary, T., Perry, S. 2005. General chemistry 4th ed. Pearson Prentice Hall: Upper Saddle River, New Jersey.

Hodge H., Smith, F. 1965. Fatal human poisonings, vol. 4. Fluorine Chemistry. Academic Press : New York, New York, 2- 37.

Holmes, R., Kennedy, M. 2000. Estimation of the oxalate content of foods and daily oxalate intake. Kidney Int. 57, 1662-1667.

Hu, C.Y., Lo, S.L. and Kuan, W.H. 2003. Effects of co-existing anions on fluoride removal in electrocoagulation (EC) process using aluminum electrodes. Water Res. 37, 4513-4523.

Huang, C.J. and Liu, J.C. 1999. Precipitation flotation of fluoride containing wastewater from semi-conductor manufacture. Water Res. 33, 3403-3412.

Huang, R., Yang, B., Liu, Q., Ding, K. 2012. Removal of fluoride ions from aqueous solutions using protonated cross-linked chitosan particles. J. Fluorine Chem. 141, 29-34.

Islam, M., Patel, R. 2007. Evaluation of removal efficiency of fluoride from aqueous solution using quick lime. J. Haz. Mater. 143, 303-310.

Jackson, R.D., Brizendine, E.J., Kelly, S.A., Hinesley, R., Stookey, G.K. and Dunipace, A.J. 2002. The fluoride content of foods and beverages from negligibly and optimally fluoridated communities. Community Dent. Oral Epidemiol. 30, 382-91.

Jamode, A., Sapkal, V., Jamode, V. 2004. Defluoridation of water using inexpensive adsorbents, J Indian Inst. Sci. 84, 163-171.

Jedra, M., Urbanek-Karlowska, B., Fonberg-Broczek, M., Sawilska-Rautenstrauch, D. and Badowski, P. 2001. Bioavailable fluoride in poultry deboned meat and meat products, Rocz. Panstw. Zakl. Hig. 52, 225-230.

Jha, S., Singh, R., Damodaran, T., Mishra, V., Sharm, D., Deppak, R. 2013. Fluoride in groundwater: toxicological exposure and remedies. J. Toxicol. Environ. Health. 16(1), 11-25.

Jimenez-Farfan, M.D., Hernandez-Guerrero, J.C., Loyola-Rodriguez, J.P. and Ledesma-Montes, C. 2004. Fluoride content in bottled waters, juices and carbonated soft drinks in Mexico City, Mexico, Int. J. Paediatr. Dent. 14, 260-266.

Kullapa, M. 2011. Towards lessons from the field in India drinking water security. Water and Sanitation Program and Ministry of Rural Development Department of Drinking Water and Sanitation: New Delhi, India.

Kalyani, G., Rao, B. and Saradhi, V. 2009. Equilibrium and kinetic studies on biosorption ofzinc onto Gallus domesticus shell powder, J Eng. Appl. Sci. 4, 39-49.

Kishorea, M., Hanumantharao, Y. 2010. Validation of defluoridation method with “acacia arabica”plant byproduct through 2nd factorial experimentation-statistical approach. Inter. J. Appl. Bio. Pharma. Technol. 1(3), 1230-1235.

Krishnamachari, K.A. 1976. Further observations on the syndrome of endemic genu valgum of South India, Ind. J. Med. Res. 64, 284-291.

Langmuir, I. 1916. The constitution and fundamental properties of solids and liquids. J. Am. Chem. Soc. 38, 2221.

Lennon, M. 2006. One in a million: the first community trial of water fluoridation. Bulletin of the World Health Organization. 84(9) , 759-760.

Li X., Lu Q. 1990. Manufacture and use of basic calcium phosphate**.** Beijing Polytechnic University. Patent Office of China, No. CN 1,039,567 A (CL C01B25/32).

Li, L., Zhu, Z., Qui, Y., Zhang, H., Zhao, J. 2010. Adsorption of fluoride ions on a Ca-deficient hydroxyapatite. Huan Jing Ke Xue. 31, 1554-1559.

Li, Y., Zhang, P., Du, Q., Peng, X., Liu, T., Wang, Z., Xia, Y., Zhang, W., Wang, K., Zhu, H., Wu, D. 2001. Adsorption of fluoride from aqueous solution by graphene. J. Colloid Interface Sci. 363, 348-354.

Lin, J., Raghavan, S., Fuerstenau, D. 1981. The adsorption of fluoride ions by hydroxyapatite from aqueous solution. Coll. Surf. 3, 357-370.

Lislie, A.L. 1967. Means and methods of defluoridation of water. U.S. Patent No. 3,337,453.

Loberg, A., Yee, H., 2016. Titration of a Weak Polyprotic Acid. NSF and UC Davis : Chemistry LibreTexts.https://chem.libretexts.org/Core/Analytical_Chemistry/Lab_Techniques/Titration/ Titration_Of_A_Weak_Polyprotic_Acid.

Lounici, H., Addour, L., Belhocine, D., Grib, H., Nicolas, S., Bariou, B., Mameri, N. 1997. Study of a new technique for fluoride removal from water. Desalination. 114, 241-251.

Lu, Y., Sun, Z., Wu, L., Wang, X., Lu, W., Liu, S. 2000. Effect of high-fluoride water on intelligence in children. Fluoride. 33(2), 74-78.

Lung, S.C., Cheng, H.W. and Fu, C.B. 2007. Potential exposure and risk of fluoride intakes from tea drinks produced in Taiwan. J. Expo. Sci. Environ. Epidemiol. 18, 158-166.

Lutgens, F., Tarbuck, E. 2000. Essentials of Geology, 7th ed. Prentice Hall: Upper Saddle River, New Jersey.

Maiti, A., Basu, J., De, S. 2011. Chemical treated laterite as fluoride adsorbent for aqueous system and kinetic modelling, Desalination. 265, 28–36.

Majima, T., Takatsuki, H. 1987. Fluoride removal from smoke-washing wastewater by using CaF_2 separating method. Water Purif. Liq. Wastes Treat. 28, 433.

Maliyekkal, S., Sharma, A., Philip, L. 2006. Manganese-oxide-coated alumina: a promising sorbent for defluoridation of water, Water Res. 40, 3497-3506.

Manji, F., Kapila, S. 1986. Fluorides and fluorosis in Kenya: the occurrence of fluorides. Odontostomatol. Trop. 9(1), 15-20.

McCaffrey, L.P., Willis, J.P. 2001. Distribution of fluoride-rich groundwater in the eastern and Mogwase regions of the northern and north-west provinces. W.R.C. Report. No.526/1/01.

McCann, H., 1968. The solubility of fluorapatite and its relationship to that of calcium fluoride. Archs. Oral Bid., 13, 987-1001.

Meenakshi, Maheshwari, R. 2006. Fluoride in drinking water and its removal. J. Haz. Mat. 137, 456-463.

Mekonen, A., Kumar, P. and Kumar, A. 2001. Integrated biological and physicochemical treatment process for nitrate and fluoride removal. Water Res. 35, 3127-3136.

Mintz, E., Reiff, F., Tauxe, R. 1995. Safe water treatment and storage in the home: A practical new strategy to prevent waterborne disease. JAMA. 273, 948-953.

Mjengera, H. and Mkongo, G. 2003. Appropriate deflouridation technology for use in flourotic areas in Tanzania. Phys. Chem. Earth, 28, 1097-1104.

Mohapatra, M., Anand, S., Mishra, B., Giles, D., Singh, P. 2009. Review of fluoride removal from drinking water. J. Environ. Manage. 91, 67-77.

Mourabet, M., El Boujaady, H., El Rhilassi, A., Ramdane, H., Bennani-Ziatni, M., El Hamri, R., Taitai, A. 2011. Defluoridation of water using brushite: equilibrium, kinetic and thermodynamic studies. Desalination. 278, 1-9.

Mourabet, M., Rhilassi, A., Boujaady, H.E., Bennani-Ziatni, M., Hamri, R., Taitai, A. 2012. Removal of fluoride from aqueous solution by adsorption on hydroxyapatite using response surface methodology. J. Saudi Chem. Soc. http://dx.doi.org/10.1016/j.jscs.2012.03.003.

MRD. 2004. First report: standing committee on rural development. Ministry of Rural Development (Department of Drinking Water Supply) : New Delhi, India. 33.

Murutu, C., Onyango, M., Ochieng, A., Otieno, F. 2012. Fluoride removal performance of phosphoric acid treated lime: Breakthrough analysis and point-of-use system performance, Water SA. 38, 279–285.

Nair, K., Manji, F.,Gitonga, J. 1984. The occurrence and distribution of fluoride in groundwaters in Kenya, challenges in African hydrology and water resources. IAHS Publ. 144, 75-86.

Nakkeeran, E. and Sitaramamurthy, D.V. 2007. Removal of fluoride from ground water, Can. J. Pure Appl. Sci. 1, 79-82.

Nath, S., Dutta, R. 2010. Fluoride removal from water using crushed limestone. Ind. J. Chem. Technol. 17, 120-125.

Nath, S., Dutta, R. 2012. Acid-enhanced limestone defluoridation in column reactor using oxalic acid. Process Safety Environ. Prot. 90, 65-75.

Nath, S., Dutta, R. 2015. Significance of calcium containing materials for defluoridation of water: a review. Desalin. Water Treat. 53(8), 2070-2085.

Nigussie, W., Zewge, F., Chandravanshi, B. 2007. Removal of excess fluoride from water using waste residue from alum manufacturing process. J. Hazard. Mater. 147, 954-963.

Noonan, S., Savage, G.1999. Oxalate content of foods and its effect on humans. Asia Pacific J. Clin. Nutr. 8, 64-74.

Oguz, E., 2005. Thermodynamic and kinetic investigations of $PO4^{3-}$ adsorption on blast furnace slag, J. Colloid. Interf. Sci. 62, 281.

OI Analytical. 2014. Fluoride, USGS by ISE and FIA, method abstract, flow solution 3100. OI Analytical: College Station, Texas.

Ozsvath, D.L. 2009. Fluoride and environmental health: a review. Rev. Environ. Sci. Biotechnol. 8, 59-79.

Pearce E., Larsen M. 1993. Defluoridation of drinking water by coprecipitation with apatite. Caries Research. 27, 378-386.

Peavy, S.H., Rowe, R.D. and Tchobanoglous, G. 1985. Environmental Engineering, International Edition. 134-135. McGraw-Hill Book Co.: Singapore.

Poiner, G., Ghosh, M., Ng, Y, Issa, T., Anand, S., Singh, P. 2011. Defluoridation behavior of nanostructured hydroxyapatite synthesized through an ultrasonic and microwave combined technique. J. Hazard. Mater. 185, 29-37.

Queste, A. 2001. High concentrations of fluoride and boron in drinking water wells in the Muenster region - results of a preliminary investigation. Int. J. Hyg. Environ. Health. 203, 221-224.

Qureshi, N. and Malmberg, R.H. 1985. Reducing aluminum residuals in finished water, J. AWWA. 77, 101-108.

Raichur, A., Basu, M. 2001. Adsorption of fluoride onto mixed rare earth oxides. Sep. Purif. Technol. 24, 121-127.

Rajiv Gandhi National Drinking Water Mission. 1993. Prevention and control of fluorosis in India. Gandhi National Drinking Water Mission Manual. RGNDWM: New Delhi, India.

Ramanathan, P. 2004. An overview of fluoride addition in contamination of drinking water : methods of estimation and removal. National Seminar on Fluoride and Arsenic Removal from Water: Assam, India.

Ramos, R., Ovalle-Turrubiartes, J., Sanchez-Castillo, M. 1999. Adsorption of fluoride from aqueous solution on aluminum-impregnated carbon. Carbon. 37, 609-617.

Rao, A. and Siddiqui, A.1962. Some observations on eighth nerve function in fluorosis, J. Laryng. Otol. 74, 94-99.

Rao, S. and Mamatha, P. 2004. Water quality in sustainable water management, Curr. Sci. 87, 942-947.

Reardon, E., Wang, Y. 2000. A limestone reactor for fluoride removal from wastewaters, Environ. Sci. Technol. 34, 3247-3253.

Reddy, D.R. and Deme, S.R. 2000. Skeletal Fluorosis. http://210.210.19.130/ vmul1.2/ dmr/ dmrdata/cme/fluorosis/Fluorosis.htm.

Reddy, D.R. Ravishankar, E.V., Prasad, V.S. and Muralidhar, B.N. 1994. Minor trauma causing major cervical myelopathy in fluorosis, ICRAN 94, Gold Coast. 585-586.

RGNDWM. 2001. Making water safe; two user friendly methods to deal with the scourge of fluorosis, Jalavani-newsletter on rural water and sanitation in India. RGNDWM and Water and Sanitation Program: South Asia WSP-SA. 3, 7.

Sawilska-Rautenstrauch, D., Jedra, M., Fonberg-Broczek, M., Badowski, P. and Urbanek-Karlowska, B. 1998. Fluorine in vegetables and potatoes from the market in Warsaw, Rocz. Panstw. Zakl. Hig., 49, 341-346.

Saxena, V. and Ahmed, S. 2001. Dissolution of fluoride in ground water: a water-rock interaction study, Environ. Geol., 40, 1084-1087.

Saxena, V. and Shakeel, A. 2003. Inferring the chemical parameters for the dissolution of fluoride in ground water, Environ. Geol. 43, 731-736.

Schoeman, J.J. and MacLeod, H. 1987. The effect of particle size and interfering ions on fluoride removal by activated alumina, Water SA. 13, 229-234.

Segreto, V., Collins, E., Camann, D., Smith, C., 1984. A current study of mottled enamel in Texas. JADA. 108 (1), 56-59.

Shan, G., Rong, S., Wei, Z., Haiyan, Z., Huixin, L., Feng, H. 2009. Size-dependent defluoridation properties of synthetic hydroxyapatite. J. Fluorine Chem. 130,550-556.

Shen, F., Chen X., Gao, P., Chenet, G. 2003. Electrochemical removal of fluoride ions from industrial wastewater. Chem. Eng. Sci. 58, 987-993.

Singano, J. Mashauri, D., Dahi, E., Matalo, F. 1997. Effect of pH on defluoridation of water by magnesite. Proceedings of the First International Workshop on Fluorosis and Defluoridation of Water, 18-22.

Singh, P.P., Barjatiya, M.K., Dhing, S., Bhatnagar, R., Kothari, S. and Dhar, V. 2001. Evidence suggesting that high intake of fluoride provokes nephrolithiasis in tribal populations, Urol. Res. 29, 238-244.

Sobsey, M., Stauber, C. 2008. Point of use household drinking water filtration: a practical, effective solution for providing sustained access to safe drinking water in the developing world. Environ. Sci. Technol. 42 (12), 4261-4267.

Spak, C. Sjostedt, S., Eleborg, L., Veress, B., Perbeck, L., Ekstrand, J.1989. Tissue response of gastric mucosa after ingestion of fluoride. Brit. Med.J. 298, 1686-1687.

Spinelli, M., Brudevold, F., Moreno, E. 1971. Mechanism of fluoride uptake by hydroxyapatite. Arch. Oral. Biol. 16, 187-203.

Srimurali, M., Pragathai, A., Karthikeyan, J. 1998. A study on removal of fluoride from drinking water by adsorption onto low-cost materials. Environ. Pollut. 99, 285-289.

Subba, R. and John, D. 2003. Fluoride incidence in ground water in an area of Peninsular India, Environ. Geol. 45, 243-251.

Sujana, M., Padhan, H., Anand, S. 2009. Studies on sorption of some geomaterials for fluoride removal form aqueous solutions. J. Hazard Mater. 2009. 161, 120-125.

Sujana, M., Thakur, R., Rao, S. 1998. Removal of fluoride from aqueous solution by using alum sludge. J. Colloid Interface Sci. 206, 94-101.

Susheela, A. 1989. Fluorosis: early warning signs and diagnostic test. Nutrition Foundation of India: New Delhi, India. 10(2).

Susheela, A. 1995. Epidemiological studies of health risks from drinking water naturally contaminated with fluoride. IAH. 233, 123-134.

Susheela, A. 2003. A treatise on fluorosis, revised 2nd edn. Fluorosis Research and Rural Development Foundation: New Delhi, India.

Sushella, A. and Jethanandani, P. 1996. Circulating testosterone levels in skeletal fluorosis patients, Clin. Toxicol. 34, 183-189.

Taher, M., Ahmed, P. 1998. Geography of north-east India , El-Dorado Publications: Guwahati, India.

Tantijaroonroj, A., Lauprasert, P. and C. Phornpimolthape, C. 2009. The Fluoride Removal in Water by Egg Shell, Activated Carbon, and Rice Husk Ash. KKU J. Pub. Health Res. 2, 55-62.

Thippeswamy, H.M., Kumar, N., Anand, S.R., Prashant, G.M. and Chandu, G.N. 2010. Fluoride content in bottled drinking waters, carbonated soft drinks and fruit juices in Davangere city, India, Indian J. Dent. Res. 21, 528-530.

Tekle-Haimanot, R., Melaku, Z., Kloos, H., Reimann, C., Fantaye, W., Zerihun, L., Bjorvatn K. 2006. The geographical distribution of fluoride in surface and groundwater in Ethiopia with an emphasis on the Rift Valley. Sci. Total Environ. 367(1), 182-190.

Thermo Scientific. 2011. Fluoride ion selective electrode user guide. Thermo Scientific Inc.: Waltham, MA.

Thole, B., Mtalo, F., Masamba, W. 2012. Groundwater defluoridation with raw bauxite, gypsum, magnesite, and their composites. Clean - Soil Air Water. 40, 1222–1228.

Thomas, A. and James, R. 2013. Accumulation of fluoride in etroplus suratensis, oreochromis mossambicus and anabas testudineus caught from the surface fresh water sources in Alappuzha town, Kerala, India, Int. J. Innov. Res. Sci. Eng. Technol. 2, 2756-2761.

Trikha, R., Sharma, B. 2014. Studies on factors affecting fluoride removal from water using passive system. J. of Env. Chem. Eng. 2, 172-176.

Trivedi, M., Verma, R., Chinoy, N., Patel, R., Sathawara, N. 2007. Effect of high fluoride water on intelligence of school children in India, Fluoride. 40, 178-183.

Turner, A., Binning, P., Stipp, S. 2005. Fluoride removal by calcite: evidence for fluoride precipitation and surface adsorption, Environ. Sci. Technol. 39, 9561-9568.

Turner, B., Binning, P., Stipp, S. 2010. Impact of phosphate on fluoride removal by calcite, Environ. Eng. Sci., 27, 643-650.

UNICEF. 1999. State of the art report on the extent of fluoride in drinking water and the resulting endemicity in India. Fluorosis Research & Rural Development Foundation for UNICEF: New Delhi, India.

UNICEF and WHO. 2012. Progress on drinking water and sanitation: 2012 update. WHO Press: Geneva, Switzerland.

Valdez-Jimenez, L., Soria Fregozo, C., Miranda Beltran, M.L., Gutierrez Coronado, O., Perez Vega, M.I. 2011. Effects of the fluoride on the central nervous system, Neurologia. 26, 297-300.

Waghmare, S. , Arfin, T. 2015. Fluoride removal from water by calcium materials: a state-of-the-art review, IJIRSET. 4(9), 8090-8102.

Wang L., Sun X., Chang L. 1993. Screening studies on defluoridation reagents of coagulative precipitation in non-aluminium compounds. Chin. J. Con. of End. Dis. 8, 27-31.

Wang, S.X., Wang, Z.H., Cheng, X.T., Li, J., Sang, Z.P., Zhang, X.D., Han, L.L., Qiao, X.Y., Wu, Z.M. and Wang, Z.Q. 2007. Arsenic and fluoride exposure in drinking water: children's IQ and growth in Shanyin county, Shanxi province, China, Environ. Health Perspect. 115, 643-647.

WaterWorld. 2014. Largest U.S. fluoride treatment plant to receive new fluoride removal system. Penn Well Corporation: Tulsa, Oklahoma.

Weber, W. Jr. 1972. Physicochemical processes for water quality control. 199-360. A Wiley-Inter-science publication, John Wiley and Sons: New York.

Wen, D., Zhang, F., Zhang, E., Wang, C., Shuangbao, H., Zheng, Y. 2013. Arsenic, fluoride and iodine in groundwater of China. J. Geochem. Explor. 135, 1-21.

Wenming, D., Zhijun, G., Jinzhou, D., Liying, Z., Suzi, T. 2001. Sorption characteristics of zinc (II) by calcareous soil- radiotracer study. Appl. Radiat. Isotopes. 54(3), 371-375.

WHO. 2004a. Fluoride and arsenic in drinking water. World Health Organization: Geneva, Switzerland. http://www.who.int/water_sanitation_health/en/map08b.jpg.

WHO. 2004b. Fluoride in drinking-water background document for development of WHO guidelines for drinking-water quality. World Health Organization : Geneva, Switzerland.

WHO. 2005. Naturally occuring hazards, water sanitation and health, World Health Organization. Geneva, Switzerland.

WHO. 2016. Drinking water fact sheet. WHO Media Centre: Geneva, Switzerland. http://www.who.int/mediacentre/factsheets/fs391/en/.

WHO & UNICEF. 2015. Progress on sanitation and drinking water, 2015 update and MDG assessment. WHO Press: Geneva, Switzerland.

Wijesundara T. Low cost defluoridation of water using broken bricks, 30th WEDC International Conference Vientiane, Lao PDR, 2004.

Wong, M., Fung, K. and Carr, H. 2003. Aluminium and fluoride contents of tea, with emphasis on brick tea and their health implications, Toxicol. Lett. 137, 111-120.

Xiong, X., Liu, J., He, W., Xia, T., He, P., Chen, X., Yang, K. and Wang, A. 2007. Dose-effect relationship between drinking water fluoride levels and damage to liver and kidney functions in children, Environ. Res. 103, 112-116.

Yang, M., Hashimoto, T., Hoshi, N., Myoga, H. 1999. Fluoride removal in a fixed bed packed with granular calcite, Water Res. 33, 3395–3402.

Yu, W., Ningiping, C., Wei, W., Jing, C., Zhenggui, W. 2011. Enhanched adsorption of fluoride from aqueous solution onto nanosized hydroxyapatite by low molecular-weight organic acids. Desalination 276, 161-168.

Yu, X. Tong, S., Ge, M., Zuo, J. 2013. Removal of fluoride from drinking water by cellulose hydroxyapatite nanocomposites. Carbohydr. Polym. 92, 269-275.