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Abstract

Groundwater containing high concentrations of fluoride is the most common source of drinking water in rural areas in parts of east Africa, India, and China. The elevated levels of fluoride cause skeletal and dental fluorosis, which is the weakening and decay of bone structures due to the leeching of calcium from the body as calcium and fluoride bond by the process of adsorption[5]. Over 150 million people are suffering from some form of fluorosis due to the consumption of groundwater. Calcium carbonate has been demonstrated to influence fluoride removal in several forms[6]. To make fluoride removal a cost-effective and user-friendly process, a study has been done to test the efficacy of a 3D printed water filter using E.P Smartfil Filament, composed of 30% calcium carbonate and 70% PLA. The influence of varying conditions concerning the removal of fluoride from water, such as the design of the filter, time spent in contact with the filter, and initial concentration of fluoride have been investigated. The maximum amount of fluoride the filters have removed thus far from any water sample is 0.048 milligrams of fluoride per gram of calcium carbonate in the filter.

I. Introduction

Around the world, especially in rural areas of East Africa, China, and India, groundwater is a main source of drinking water and often contains a significantly high concentration of fluoride. The World Health Organization has stated that the beneficial range of fluoride for general consumption is between 0.5 mg/L and 1.5 mg/L. Consuming water that contains more than 1.5 mg/L of fluoride causes fluorosis, a condition that poses a significant threat to human health[1,3]. Fluorosis is categorized in one of two ways: skeletal or dental. Dental fluorosis presents itself as a hypocalcification with visible effects being brown stains on the teeth and deformation of the jaw structure (**Figure** 1)[2]. As high levels of fluoride accumulate, calcium is leeched from teeth and jaw bones forming a layer calcium fluorapatite around the structure of the bone. As the calcium fluorapatite breaks down, and fluoride continues to be consumed, calcium is leeched from the bone in excess, causing the resulting physical deformities. When fluoride levels reach above 5 mg/L, skeletal fluorosis begins to occur, following the same leeching process as dental fluorosis except on bones throughout the body. Some physical defects of skeletal fluorosis include an increase in bone mass and density, and the development of cartilaginous lesions (**Figure 1**)[2]. Non-skeletal effects include gastrointestinal irritation and destruction of filaments in muscle tissue. Populations that are exposed to high levels of fluoride in groundwater are the most likely to suffer from skeletal and dental fluorosis. Around the world, over 150 million people suffer from some form of fluorosis due to the consumption of over-fluoridated groundwater. A majority of the populations affected by the debilitating effects of fluorosis are impoverished and do not have access to large-scale water treatment systems. Due to this, there is a need to develop a low-cost method for removing fluoride from drinking water down below the limit set by the World Health Organization (1.5 mg/L).

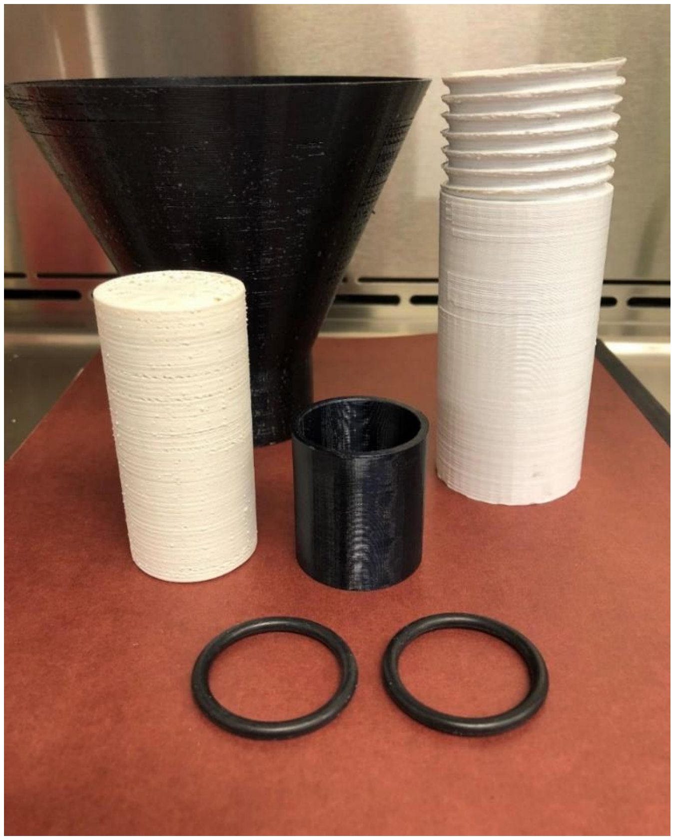
Figure 1: *(left) A beginning look at dental fluorosis with mild staining of the teeth. (from Mosby's Medical Dictionary) (right) Severe skeletal fluorosis, showing deformed legs as a result of bone decay (from http://bellabonezblog.blogspot.com/2016/04/skeletal-fluorosis.html)*

Calcium carbonate has been shown to remove fluoride from over-fluoridated water in several forms[4]. When in contact with fluoridated water, calcium carbonate acts as an adsorbent. Adsorption is the process by which a solid holds liquid or gas molecules in a thin film around the surface of the solid[7]. The objective of this research is to combine the adsorption method of fluoride removal with 3D printing technology through the creation of a calcium carbonate-based filter. 3D printing requires two main components, a model created using design software and the printer itself. The filter designs were altered based on testing to maximize the contact of the water with the surface area of the filter and increase contact time in the filter. To print the design, the design is uploaded from a computer onto the printer, where filament is threaded through a heated extruder. The heated extruder moves over the top of a buildplate in the shape of the desired design, and the melted filament, which is generally a plastic material, quickly hardens. This method of 3D printing is known as fused deposition modeling. In this case, a filter system have been created using E.P smartfil filament, composed of 30% calcium carbonate and 70% PLA. PLA, or Polylactic Acid is a commonly used non-toxic, plastic 3D printing filament. This filter will require no hazardous chemicals or special operational use, making it ideal for use by local people where over-fluoridated groundwater is the only accessible drinking water.

II. Materials and Methods

Autodesk's Fusion 360 design software was used to create the designs for the funnel system and filters, which includes a siphon funnel, holder for the filter, and a spacer (**Figure 3**). Rubber o-rings were used in the implementation of the system as a seal. The first design of the filter was printed using the technique of under-extrusion. One-millimeter coils were implemented in the second design of the filter. The third design of the filter included cylindrical rings and a 25-millimeter layer of filament acting as a microparticle filter. The printed filters have a height of 76 millimeters and diameter of 35 millimeters. The siphon funnel held 500 milliliters.

Figure 3: *The pieces of the funnel system, including the siphon funnel, holder for the filter, spacer, and rubber o-rings, along with one of the filters.*



To test the volume of solution needed to active the siphon of the funnel, 150 milliliters of water was added to the funnel, then water was added in 5 mL increments until the water began to flow through the funnel. To determine the volume of solution lost to the system, 500 milliliters of water were flowed through the funnel into a beaker and the volume in the beaker was recorded and subtracted from the initial 500 milliliters. Both processes were repeated three times.

The efficacy of the printed filters was tested by cycling fluoridated samples of water through the funnel system. Stock solutions of fluoridated water at 5 mg/L, 8 mg/L, and 10 mg/L were made using 0.1 M sodium fluoride and deionized water. 20 milliliter samples of each stock solution were taken for testing. 350 milliliters of the 5 mg/L stock solution was poured through the filter system. After one cycle, a 20-milliliter sample was removed, and the remaining solution was poured through the funnel system again.

This process was repeated three times for each filter. The cycling process was repeated using the 8 mg/L and 10 mg/L concentrations of stock solution. This process was repeated five times.

The effect of time on the removal of fluoride by the filters was tested using a peristaltic pump system. A 10 mg/L stock solution of fluoridated water was made using 0.1 M sodium fluoride and deionized water. A 20-milliliter sample was taken for testing. 500 milliliters of the stock solution was flowed at 150 milliliters per second using a peristaltic pump system through the filter without the siphon funnel attached. 20-milliliter samples were taken after 1 hour, 3 hours, and 24 hours. The concentration of fluoride in the samples removed from both cycle testing and the time tests was measured using an Extech Fluoride Meter and ThermoFisher Orion Ion Selective Electrode.

To observe the contact of the water with the surface area of the filters, a cross-sectional dye analysis was performed. A solution of direct red dye was made and flowed through the funnel system. The filter was removed from the system and left out to dry. When dry, the filter was split in half and observations were made regarding the flow of the water through the filter. This process was repeated for each design of the filter.

III. Results

It was found that 180 milliliters of solution was needed to activate the siphon funnel and 9.5 milliliters of solution was lost to the system. The data displayed in figures 6 and 7 is represented as mg of fluoride removed per gram of calcium carbonate contained in the filter; found using the equation: $\frac{x}{m} = \frac{(C_o - C_f)(V)}{m}$, where $C_o - C_f$ is the initial and final concentrations of fluoride, V is the volume of solution, and m is the mass of calcium carbonate.

Figure 4: *shows a breakdown of the design of each filter, with design 1 being the implementation of the under-extruded technique, design 2 being the filter with 1-millimeter coils, and design 3 being the cylindrical rings and addition of a "microfilter". (From left to right: Design 1, Design 2, and Design 3) The attached chart shows which filter was the implementation of which design.*

Filter Design	**1** 	**2** 	**3** 
Filter Numbers	**1, 2, 3, 4, 5, 6, 7**	**8, 9, 10, 11, 12, 13, 14**	**15, 16, 17, 18, 19, 20**

Figure 5: *Graph showing the removal of fluoride after two cycles through the funnel system in milligrams of fluoride removed per gram of calcium carbonate contained in the filter. Samples were taken for testing after 3 cycles, but the removal of fluoride by the third cycle was negligible. Data from filters 3 and 4 is omitted due to contamination of samples.*

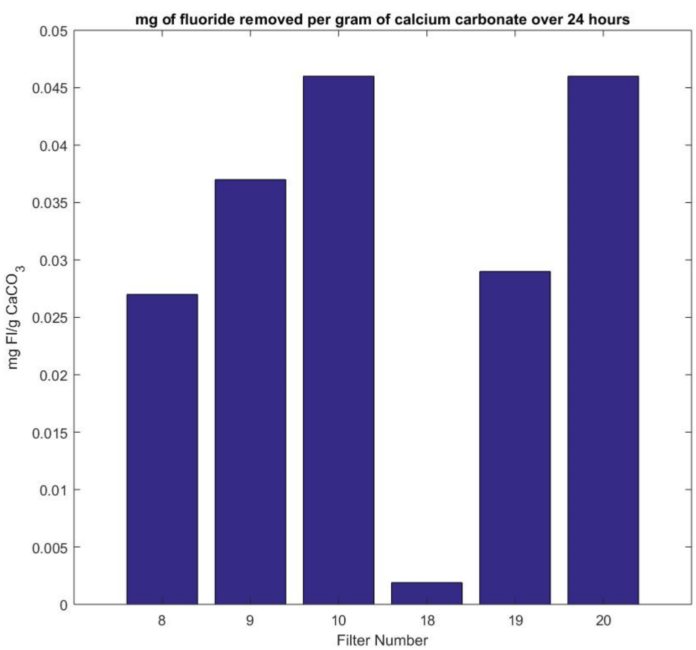
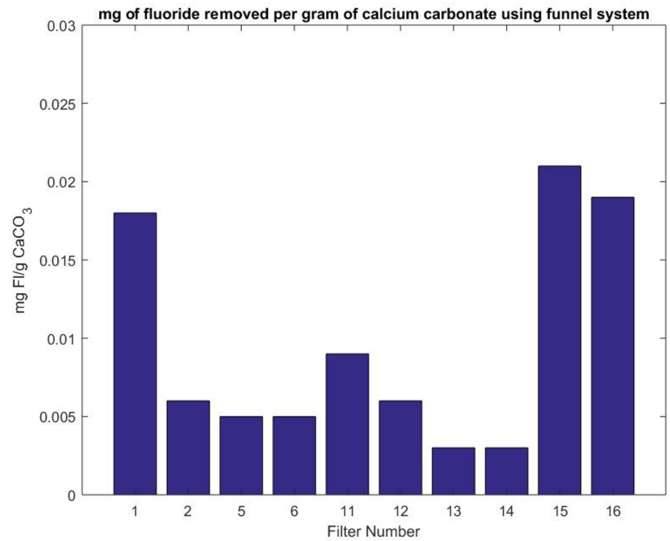


Figure 6: *Graph showing the removal of fluoride after 24 hours by the filters using the peristaltic pump system. Samples were taken after 1 hour, 3 hours, and 24 hours to observe if there were any changes in the rate of removal of fluoride by the filters over time. Data from filters 7 and 17 is omitted due to an error accounting for the volume loss due to evaporation in the pump system.*



IV. Conclusions

The goal of creating the calcium carbonate filters was to remove fluoride from water in order to prevent the onset of fluorosis due to consumption of over-fluoridated groundwater. After initial tests showed that the filters were capable of removing fluoride, the filter design was improved in order to maximize contact of the water with surface of the filter and maximize the amount of time the water remained in the filter. Cross-sectional analysis of the filters showed that the flow of water through the initial design was limited to the middle of the filter. The coiled design showed an improvement in surface area contact while the cylindrical design showed an improvement in both surface area contact and time spent in the filter. Initially, there was speculation that there was a relationship between the initial concentration of fluoride and the amount of fluoride removed. Our results thus far show no qualitative relationship between the two.

The maximum removal of the filters was 0.048 milligrams of fluoride per gram of calcium carbonate in the filter; this removal occurred after 24 hours in the peristaltic pump system. On average after 2 cycles, the filters removed 0.01 milligrams of fluoride per gram of calcium carbonate. While some removal did occur, the removal thus far would not decrease the likelihood of a person suffering from fluorosis after drinking the filtered water.

V. Future Work

Although initial tests have shown that the filtered water would not decrease the likelihood of a person suffering from fluorosis, any removal at all is an important first step in the process of creating this filter system. In an effort to make the production of the filter system more sustainable, future work will involve the creation of calcium carbonate filament using recycled plastic and powdered calcium carbonate to print the filters. The effect of altering the flow rate and pH of the water will be tested, as well as observing the effects of the addition of other ions normally found in groundwater. The filters will continue to be redesigned to further maximize contact with the surface area of the filters.

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