

Onsite Defluoridation System for Drinking Water Treatment Using Calcium Carbonate

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Abstract

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. Advanced on-site methods, such as under sink reverse osmosis units, can remove fluoride but are too expensive for developing areas. This paper 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 a Freundlich isotherm model, and it was found that the equilibrium time was approximately 3 hours. Calcium carbonate was found to have comparable F⁻ removal abilities as the commercial ion exchange resins and possessed higher removal effectiveness compared to calcium containing eggshells and seashells. It was also found that anions, such as Cl⁻ and HCO₃⁻, 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. Through this work, we can be a step closer to bringing safe drinking water to those that do not have access to it.

Keywords

Defluoridation, on-site water treatment, calcium carbonate, fluorosis, ion-exchange

INTRODUCTION

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 (Adler et al., 1970). 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. The WHO guideline is 1.5 mg/L. However, at concentrations from 1.5 to 4 mg/L, fluoride in drinking water can cause dental fluorosis. At concentrations of 4 -10 mg/L, skeletal fluorosis can occur (WHO, 2004). Excessive fluoride in drinking water is a detrimental problem to society, causing detrimental effects to 25 nations across the world and putting 200 million people in the world at risk of fluorosis, both skeletal and dental (Jha *et al.*, 2013). Excessive fluoride causes stained teeth, bone diseases, tooth decay, stooped backs, and crooked hands and legs. Fluoride can also lead to non-skeletal fluorosis, such as harmful effects to erythrocytes, ligaments, spermatozoa, thyroid glands and destruction of filaments in the muscle tissues leading to muscle weakness. The gastrointestinal system is also adversely sensitive to fluoride in drinking water causing gastric irritation such as nausea,

vomiting and gastric pain (Spak, 1989). These detrimental side effects cause excessive fluoride to be a pollutant of concern.

Groundwater becomes contaminated with fluoride when it comes into contact with the rocks and soils that naturally contain it. 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 (Fawell *et al.*, 2006). In the United States, it has been found that 35% of the groundwater supplies in five desert regions of southern California had high concentrations of fluoride (Dawson & Belitz, 2013). In many areas of the world, a centralized water treatment plant is not available to transport clean water to households. Therefore, an on-site home treatment system that is easy to construct and maintain is necessary for these people.

LITERATURE REVIEW

Locations in the World Containing High Concentrations of Fluoride

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 that have sediments of marine origins in the mountains. An example of a geographical belt with marine origins is the mountainous regions from 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).

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 1640 mg/L in the Kenyan Lakes Elmentaita, 2,800 mg/L in the Nakuru and 690 mg/L in the Tanzanian Momella soda lakes (Nair *et al.*, 1984). There is also high volcanic activity in Nairobi, Rift Valley and Central Provinces with fluoride groundwater concentrations of 30-50 mg/L. There are many instances of dental fluorosis in this area, with concentrations in the Rift Valley up to 45 mg/L (Manji and Kapili, 1986).

Groundwater can also be contaminated with fluoride when it comes into contact with rocks and soils that naturally contain fluoride. Locations that have contaminated groundwater include Southern and West Africa, China, 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, endemic fluorosis has been observed in all 28 provinces except for Shanghai, especially those with deep groundwater. In Sri Lanka, fluoride concentrations can be found up to 10 mg/L in groundwater in areas that have less extensive rainfall and long-term leaching of fluoride from crystalline bedrock (Fawell *et al.*, 2006). In India, 17 out of the 32 states were found with high concentration of fluoride (UNICEF, 1999). The states with the highest levels of fluoride include: “Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh,” with the highest concentration found in the Rewari District of Haryana of 48 mg/L (UNICEF, 1999).

There has been fluoride concentrations found in the United States' groundwater that have caused dental fluorosis since the 1930's. In Colorado Springs, they first named the problem to be "mottled enamel" or "Colorado brown stain." In 1930, it was found that the fluoride in drinking water was the cause of the "mottled enamel" and the problem was renamed fluorosis. Historically, endemic fluorosis has been reported in "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, 1984). In the United States, it has been found that 35% of the groundwater supplies in five desert regions of southern California had high concentrations of fluoride, mainly the Antelope Valley, Coachella Valley, Owens Valley, Mojave River area, and the Colorado River basin. (Dawson & Belitz, 2013). Figure 1 shows the areas in the world predicted to have greater than 1.5 mg/L of fluoride in their groundwater.

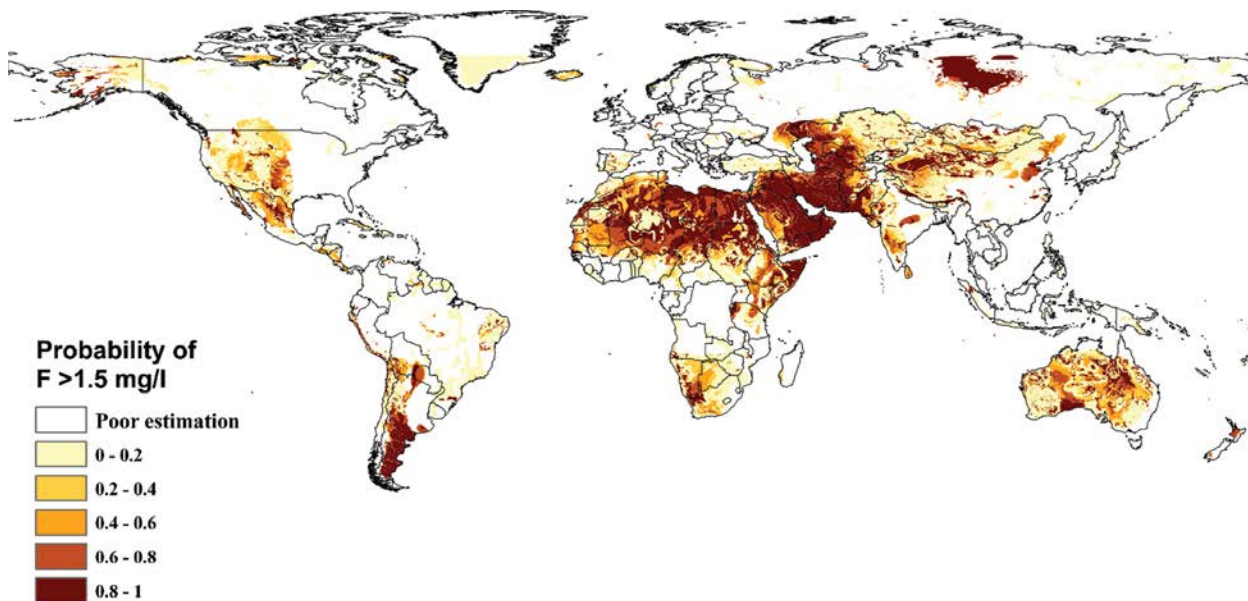


Figure 1. Predicted Probability of Fluoride Concentration in the Groundwater Exceeding WHO guideline of 1.5 mg/L (Amini *et al.*, 2008)

Current Defluoridation Treatment Systems

There are several current defluoridation methods. In developed 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 because the usage can be more variable than centralized water systems. Decentralized systems can be changed to water works, a village plant or a household system. There can be a continuous supply of defluoridated water using column filters or in batches using a water bucket. Also, we would be able to defluoridate water only used for drinking and washing, which would save resources and waste disposal (Fawell *et al.*, 2006).

Removal processes can be categorized into three main groups: 1) sorption media using bone charcoal, activated alumina and clay 2) co-precipitation chemicals using aluminum sulfate and 3) lime contact precipitations chemicals using calcium and phosphate compounds. Sorption media is preferably used in columns for a continuous supply and the media needs to be regenerated or renewed. 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. Contact precipitation chemicals are added upstream of a catalytic filter bed. There is no sludge and no saturation of the bed, only buildup of precipitate in the bed (Fawell *et al.*, 2006).

Sorption Media

Some common adsorption materials for fluoride include: “magnesite, apophyllite, natrolite, stilbite, clinoptilolite, gibbsite, goethite, kaolinite, halloysite, bentonite, vermiculite, zeolite, serpentine, alkaline soil, acidic clay, kaolinite clay, china clay, aiken soil, Fuller’s earth, diatomaceous earth, and Ando soil (Bower and Hatcher, 1967; Singano *et al.*, 1997).” These minerals all have metal lattice hydroxyl groups that can be exchanged with fluoride. An equation for a metal compound M is shown below (Fawell *et al.*, 2006):



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 (Fawell *et al.*, 2006). 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). 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 °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.

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. 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 (Fawell *et al.*, 2006).

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. 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. (Fawell *et al.*, 2006).

Co-Precipitation Chemicals

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. Aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, is added and dissolved in water using stirring and ensuring complete mixing. Aluminum hydroxide flocs are formed and settle to the bottom of the unit. Fluoride is removed by electrostatic attachment to the flocs. 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). Treatment efficiency is around 70 percent, so it may not be suitable for raw water with high fluoride contamination.

Contact Precipitation Chemicals

Contact Precipitation is when calcium and phosphate compounds are mixed with water and go through a saturated bone charcoal medium in a column filter. 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). 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). 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. The costs for calcium chloride and sodium dihydrogen phosphate was US \$283 and US \$780/ ton, respectively in 1996 (Fawell *et al.*, 2006).

Based on what we have learned from the literature review and from our experimental data, we have proposed an onsite defluoridation treatment system that can be used at home, simply built, and maintained by users. By comparing different adsorbents, such as commercial resins, seashells, eggshells and calcium pills, we have found that calcium carbonate is a promising adsorbent that has comparable fluoride removal abilities as the commercial resins. Additionally, calcium carbonate is a readily available and inexpensive adsorbent.

MATERIALS AND METHODS

Materials

Fluoride solutions were obtained by diluting a 1,000 mg/L F⁻ stock solution that was reagent grade from Thermo Scientific. Powdered calcium carbonate was attained from Fisher Scientific. The samples were measured in 50 mL Falcon tubes. SIR 900 and SBG2 resins were obtained from Resintech, and Amberlite IRA 400 resins were obtained from Rohm and Haas. Eggshells and seashells were air dried and then ground to a powder using a blender.

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. 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.

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 (with and without blending). 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:

$$x/m = (C_0 - C_t)V/m \quad (2)$$

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:

$$\ln q = \ln(K) + \frac{1}{n} \ln(C) \quad (3)$$

where q is the x/m value as stated above, C is the concentration of fluoride and K is a constant. $\ln(q)$ was plotted against $\ln(C)$ to determine the slope, which is $\frac{1}{n}$.

Methods for Selectivity Experiments

Selectivity experiments have been performed so far using only one media, the SIR 900 media. 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 167 mg/L Cl^- concentration. Batch studies were performed for SIR 900 media added at 0.7 & 2.0 grams. x/m values (amount of fluoride adsorbed by the media) were plotted against mg/L Cl^- .

Methods for Equilibrium Experiments

The time for the samples to reach equilibrium was determined. Varying amounts of calcium carbonate were put into 1,000 mL Erlenmeyer flasks and filled with 5.6 mg/L of fluoride solution: 0.11g, 0.21 g, 0.4 g, 0.57 g. We then shook the samples for 403 minutes at 100 rpm and took samples from the Erlenmeyer flasks at different time intervals. We measured the fluoride concentrations using the ion selective electrode and graphed concentration of fluoride versus time.

Methods of 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. The columns were 2.5 cm in diameter and 35 cm long, containing approximately 95 grams of CaCO₃ 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 from 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.

$$\text{Single Column : } \frac{x}{m} = \sum_0^t Q \frac{C_0 - C_t}{m} \quad (4)$$

$$\text{Column in Series: } \frac{x}{m} = \frac{\sum \left(\sum_0^t Q \frac{C_0 - C_1}{m_1} + \sum_0^t Q \frac{C_1 - C_2}{m_2} + \sum_0^t Q \frac{C_2 - C_3}{m_3} \right)}{\text{number of columns}} \quad (5)$$

where Q is the flow rate (mL/min), C₀ 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).

RESULTS

Batch & Isotherm Experiment for Different Adsorbents

Figure 2 shows x/m (mg/g) values of different adsorbents plotted against fluoride concentration to compare experimental isotherms for each of the adsorbents. At a concentration of 1.5 mg/L of fluoride, x/m values for SIR 900, commercial calcium pill 1, calcium carbonate, SBG2, eggshell, Amberlite, commercial calcium pill 2 and seashells were 0.08, 0.065, 0.035, 0.019, 0.005, 0.0046 and 0.0017 respectively. For calcium carbonate, the best-fit values of K and n for the Freundlich isotherm are 0.03 and 1.94, respectively, and are also shown as the smooth line in Figure 2.

Selectivity Experiment

The first selectivity experiment using SIR 900 showed negligible impact of chloride on fluoride adsorption.

Calcium Carbonate Experiments

For the equilibrium experiment, we plotted concentration of fluoride against time for different amounts of calcium carbonate. We found that the equilibrium time occurred at approximately 180 minutes.

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). 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.

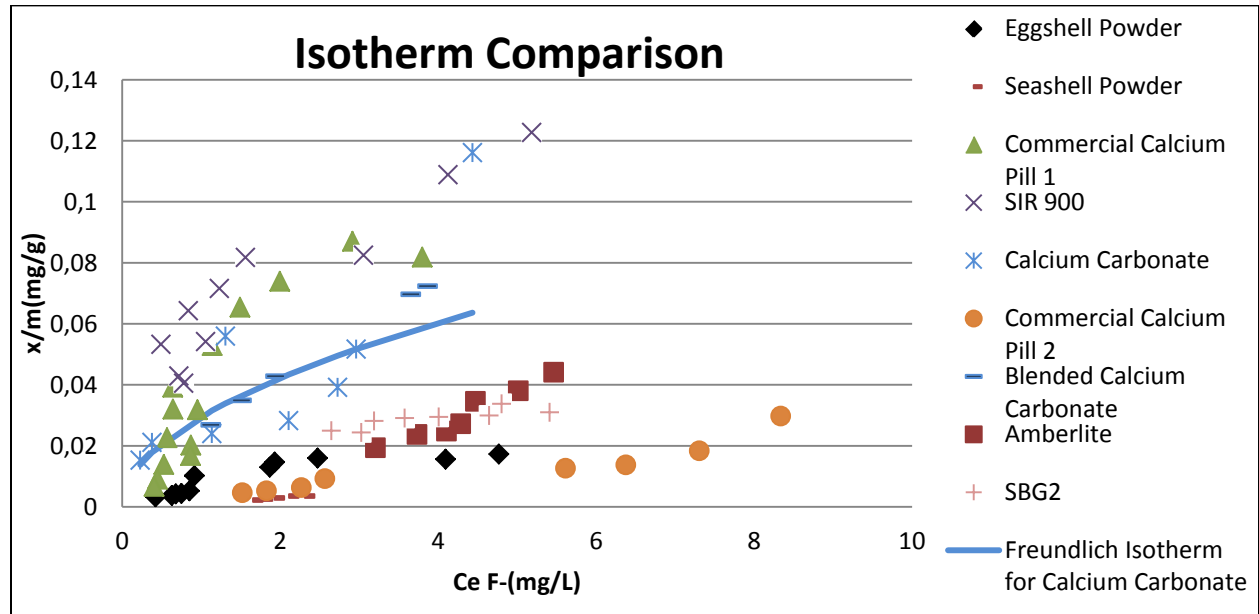


Figure 2. Experimental Isotherm Comparison among Different Adsorbents.

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 column 3 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 335.55 mL. For column 2 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 221.71 mL. For column 1 at 1.5 mg/L of fluoride, the x/m value was 0.0091 mg/g, time was 149.2 minutes and volume of water treated was 55.26 mL (Figure 4).

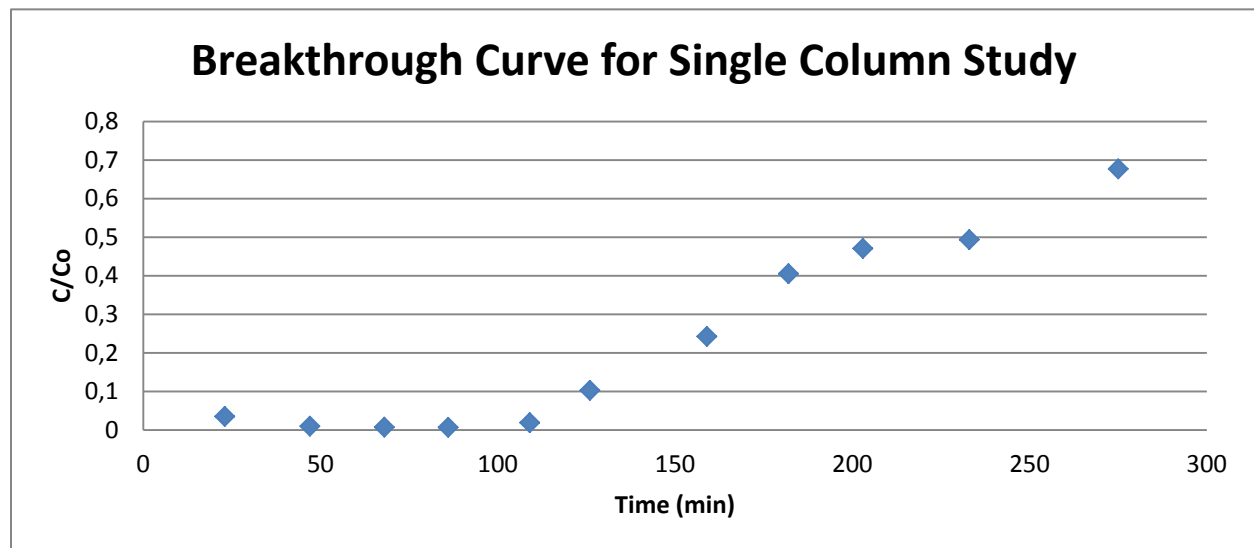


Figure 3. Breakthrough Curve Using a Single Column Containing Calcium Carbonate

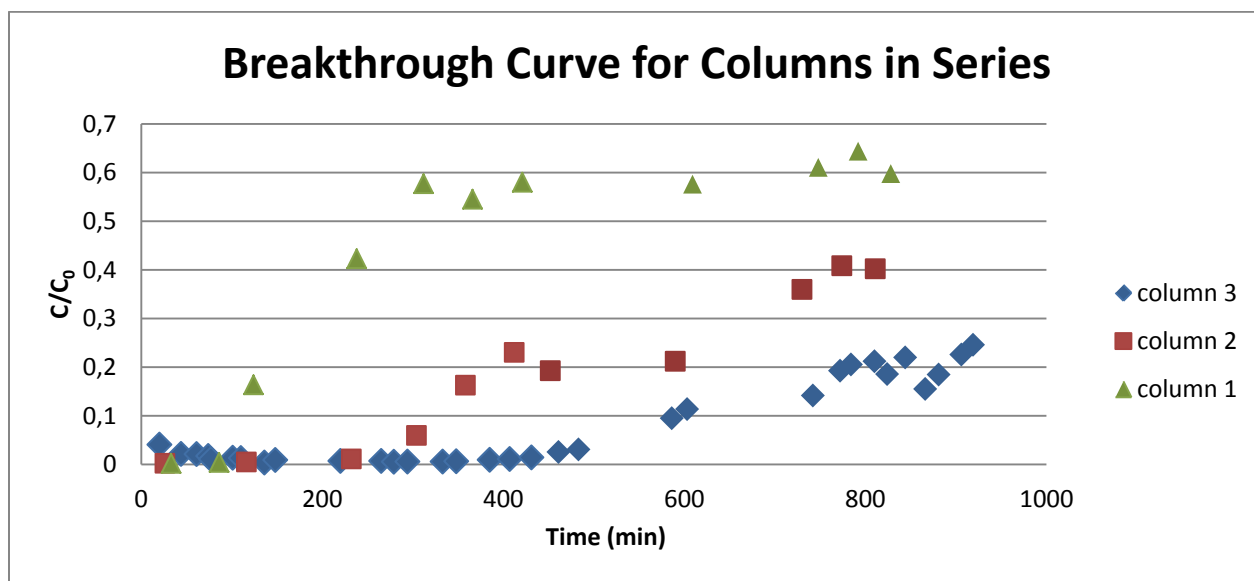


Figure 4. Breakthrough Curve Using Three Columns in Series Containing Calcium Carbonate

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 5 to 7 mg/L.

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, easy to use and maintainable by users. In this study, we looked at different adsorbents to use in our defluoridation system. After performing a series of isotherm experiments comparing different adsorbents, we chose calcium carbonate as the adsorbent to use, since it is relatively inexpensive and has comparable defluoridating abilities to the commercial adsorbents. In our batch studies, we determined that the x/m value for calcium carbonate was 0.035 mg/g and that the equilibrium time was at approximately 180 minutes. In the column studies, we determined that the x/m value for the single column study was 0.011 mg/g and 0.38 mg/g 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. For future studies, we will analyze ways to make this onsite treatment system more effective, such as using phosphate in the column system, as well as performing more selectivity tests. Through this study, we can be a step closer to providing an accessible onsite defluoridation treatment system to places in need.

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