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Research article

# Onsite defluoridation system for drinking water treatment using calcium carbonate

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ABSTRACT

Fluoride in drinking water has several effects on 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 reserve osmosis units, can remove fluoride but are too expensive for developing areas. This paper investigates 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 h. 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 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. Through this work, we can be a step closer to bringing safe drinking water to those that do not have access to it.



## 1. 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 in 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). Observable symptoms of excessive fluoride include 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 affected by high fluoride ingestion causing gastric irritation such as nausea, vomiting and gastric pain (Spak et al., 1989). These detrimental side effects cause excessive fluoride to be a pollutant of concern.

Fluoride occurs naturally in all waters. Excessive fluoride can also be found in large geographical belts in the mountains that have sediments of marine origins and in geographical belts that have volcanic activity, such as the mountainous regions from Iraq and Iran to Syria and Turkey to Algeria and Morocco and along the East African Rift from Eritrea to Malawi. Other examples include southern parts of the USA, Europe, and USSR (Fawell et al., 2006; Gupta and Ayoob, 2016; Manji and Kapila, 1986; Nair et al., 1984).

Groundwater can also be contaminated with fluoride when it

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comes into contact with rocks and soils that naturally contain fluoride. Locations that have contaminated groundwater include Southern and Western Africa, China, Thailand, Japan, Argentina, Persian Gulf states, Saudi Arabia, Europe, USA, Canada the Middle East, especially Pakistan, and southern Asia, but especially India and Sri Lanka (WHO, 2005) (Susheela, 1995). There have been fluoride concentrations found in the United States' groundwater that have caused dental fluorosis since the 1930's (Segreto et al., 1984; Dean, 1993). In the United States, it has been found that groundwater aquifers in five desert regions of southern California had high concentrations of fluoride, mainly the Coachella Valley (22%), the Colorado River basin (20%), the Mojave River area (10%), Owens Valley (3%), and the Antelope Valley (3%) (Dawson and Belitz, 2012). Groundwater can also be contaminated by fluoride through several anthropogenic industrial processes: cement and brick manufacturing, “coal fired power stations”, electronics manufacturing, aluminum smelting and refining, beryllium abstraction plants, iron smelting and producing plants, etc. (Ramanathan, 2004; Nath and Dutta, 2015; Turner et al., 2005).

There are several current defluoridation methods. Defluoridation methods 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 often packed in columns. Fluoride containing water is cycled through the columns, and the media can be regenerated, renewed or disposed. 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, acid treated 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). With adsorbents, higher removal is achieved with decreasing particle size of the adsorbent and increasing dosage (Srimurali et al., 1998), which we observed in our results. Electrochemical processes and membrane can be efficient but require power and expertise generally not available for on-site treatment in rural areas; hence, coagulation and adsorption processes are preferred. A detailed comparison is beyond our scope, but Nath and Dutta (2015) provide an extensive comparison.

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 with minimal training. 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. Broeck 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 adsorption and is reversible. Precipitation of $CaF_2$ occurs only at higher concentrations, 10–20 mg/L $F^-$ or more (Gupta and Ayoob, 2016; Nath and Dutta, 2015).

By comparing different adsorbents, such as commercial resins, seashells, eggshells and calcium pills, we have found that calcium carbonate 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).

## 2. Materials and methods

### 2.1. Materials

Fluoride solutions were obtained by diluting a 1000 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 and Sigma Aldrich, 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 size of the calcium carbonates were 100 μm. DI water was used for all the experiments.

### 2.2. 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. 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.

### 2.3. 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 Sigma Aldrich 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 h 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:

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

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 against $\frac{1}{C}$ 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:

$$\ln q = \ln qm - KD\varepsilon^2 ; \varepsilon^2 = RT\ln\left(1 + \frac{1}{C}\right) \quad (4)$$

where q is the adsorption capacity (mg/g), qm is maximum adsorption capacity (mg/g), ε is the Polanyi potential, C is the concentration (mg/L), $K_D$ $\left(\frac{mol^2}{kJ^2}\right)$ 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 $\varepsilon^2$ to determine $q_m$ and $K_D$ (Bhaumik et al., 2012; Gogoi and Dutta, 2016).

$$Es = \frac{1}{\sqrt{2K_D}} \quad (5)$$

### 2.4. 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 $Cl^-$.

### 2.5. Methods for equilibrium experiments

The time for the samples to reach equilibrium was determined. Varying amounts of calcium carbonate (0.11 g, 0.21 g, 0.4 g, 0.57 g) were placed into 1000 mL Erlenmeyer flasks and filled with 5.6 mg/L of fluoride solution. We then shook the samples for 403 min at 100 rpm 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.

### 2.6. Methods for column experiments

A single-column experiment was performed followed by column experiments consisting of 3 columns in series. Water containing 5 mg/L of fluoride for the single column experiment and 7 mg/L for the column-in-series experiments was pumped in an up flow direction through the columns using Cole-Palmer Masterflex

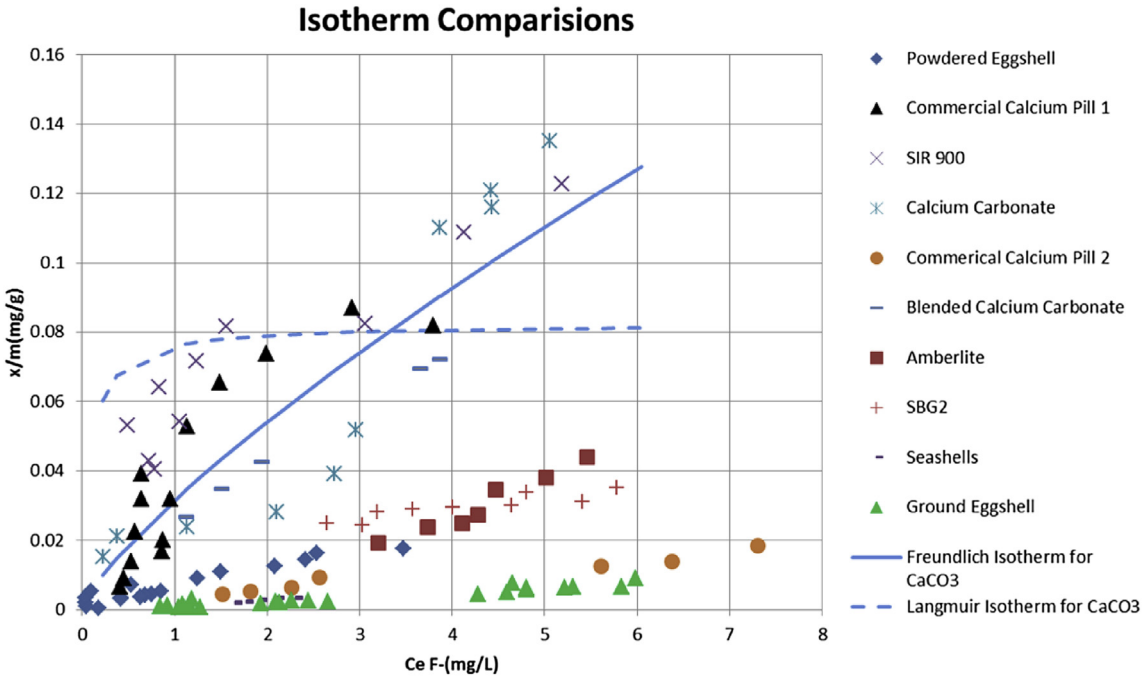


**Fig. 1.** Adsorption capacity versus fluoride concentration among commercial resins and calcium containing adsorbents with Freundlich and Langmuir isotherms.

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 (6) and (7) were used to calculate x/m values for a single column and column in series.

$$\text{Single Column}: \frac{x}{m} = \sum_{0}^{t} Q\frac{Co - C_t}{m} \tag{6}$$

$$\text{Column in Series}: \frac{x}{m} = \frac{\sum\left(\sum_0^t Q\frac{Co-C1}{m_1} + \sum_0^t Q\frac{C_1-C_2}{m_2}\sum_0^t Q\frac{C2-C3}{m_3}\right)}{number\ of\ columns} \tag{7}$$

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. Results and discussion

### 3.1. Batch & isotherm experiment for different adsorbents

Fig. 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 Fig. 1. Table 1 shows different adsorption values for the 10 adsorbents used at 1.5 mg/L. Table 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. Note also that lowering the 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 at lower pH (Turner et al., 2005; Yang et al., 1999).

**Table 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 |
| Eggshells | 0.012 |
| Amberlite IRA 400 | 0.005 |
| Commercial Calcium Pill 2 | 0.0046 |
| Seashells | 0.0017 |
| Ground Eggshells | 0.00095 |

**Table 2**
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. 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 (Supplementary Materials). This is important 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 (0.1 g, 0.2 g, 0.4 g and 0.56 g). We found that the equilibrium time occurred at approximately 180 min (Supplementary Materials).

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 min 72.3 mL of water could be treated with a single column using approximately 95 grams of calcium carbonate (Supplementary Materials). We would need 2.6 kg of calcium carbonate to attain 2 L of defluoridated water, which is the average amount of water a person would drink per day.

We improved 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 min, 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 min 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 min and volume of water treated was 55.3 mL (Supplementary Materials). 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 kg of calcium carbonate to attain 2 L of defluoridated water having an initial concentration of approximately 7 mg/L, and significantly less calcium carbonate at lower concentrations.

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. (2016) 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 bring down 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.

## 4. 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 min. 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 kg of calcium carbonate to defluoridate 2 L 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.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2017.06.060.

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