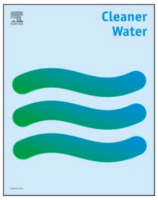
Cleaner Water 2 (2024) 100025

Contents lists available at ScienceDirect

Cleaner Water

journal homepage: www.sciencedirect.com/journal/cleaner-water



Coral sands as potential low cost treatment for removing fluoride from drinking water

M.H. Lecompte [a,*,1], B. Robinson [b], S. Gaw [b]

[a] Waterways Centre, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand
[b] School of Physical & Chemical Sciences, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand

ABSTRACT

Fluoride (F-) toxicity from contaminated drinking water affects over 200 million people worldwide. While defluoridation with adsorbents such as calcium carbonate, is commonly used, most technologies are unsuitable for resource-constrained areas. Coral sand is readily available in tropical regions but is yet to be investigated as a potential F- adsorbent. The effectiveness of coral sand at removing F- from drinking water was assessed using acid-enhanced lime defluoridation with two beach (Kiribati and Vanuatu) and one commercially available coral sands. Citric acid was selected as it is readily accessible, palatable and safe for human consumption. Mini columns with a 5:1 sand-to-fluid ratio, 0.025 M citric acid and a 4-hour residence time, could be used seven times to reduce F- from 10 mg/L to below the World Health Organization (WHO) guideline value of 1.5 mg/L. Mini columns packed with coarser grained (1.3 mm) Vanuatu sand could be used at least 10 times. Increasing citric acid to 0.050 M reduced removal efficiency. Prototype treatment devices, developed using 1 L polyethylene jerrycans and 1 kg of commercial sand, could only be used a maximum of three times with 0.025 M citric acid. All coral sands contained F- as well as other trace elements of human health concern, including As, B, Cr, Mn, and Ni that were released into the treated water, resulting in exceedances of drinking water standards. Total Cr concentrations in treated water always exceeded the 0.05 mg/L WHO health guideline whereas As exceeded the 0.01 mg/L value in the majority of treated water samples. In addition, B, Na, and Ni concentrations exceeded the WHO guidelines in many water samples treated with Kiribati and Vanuatu sands. Treated water samples were also unpalatable as potable water based on hardness, total dissolved solids and elevated concentrations of Al, Fe, and Mn. It is recommended that drinking water treated with coral sand be analysed for the presence of contaminants of health concern.

1. Introduction

Excess fluoride (F^-) in drinking water is a global public health issue. Fluoride present within volcanic ash, geothermal fluids, and clay minerals derived from fluorspar (CaF_2), fluorapatite ($[3Ca_3(PO_4)2Ca(FCl_2)]$), cryolite (Na_3AlF_6) and sellaite (MgF_2), is released into soil pore water, which eventually enters drinking water (Alarcón-Herrera et al., 2013; Ayoob and Gupta, 2006; Cronin et al., 2003; Mohapatra et al., 2009; Saxena, 2018). Chronic consumption of excess F^- mainly occurs through ingesting food and water with elevated F^- concentrations, leading to fluorosis, a condition of brittle teeth and bones (Ayoob and Gupta, 2006; Allibone et al., 2012; World Health Organization., 2004; Kimambo et al., 2019). Over 200 million people are affected worldwide (Ayoob and Gupta, 2006) and the issue is particularly prevalent in low socio-economic groups (Levy, 2005), rural communities lacking central treatment systems (Kimambo et al., 2019) and areas with volcanic activity (D'Alessandro, 2006).

Where alternate water sources and better nutrition are unavailable, defluoridation of drinking water is the only viable solution (Kimambo et al., 2019; Keesari et al., 2019; Meenakshi and Maheshwari, 2006). It is mainly achieved by precipitation / coagulation, absorption, membrane technologies, or electrochemical techniques (Kimambo et al., 2019; Fan, 2003; Mohapatra et al., 2009; Yadav et al., 2018), however, such technologies are complex and costly. Precipitation is generally used for highly concentrated solutions but can only reduce concentrations to about 2 mg/L (Fan, 2003; Wang and Reardon, 2001; Yang et al., 1999; Nath and Dutta, 2010a). Fluoride may be precipitated with aluminium salt but a toxic sludge is generated (Nath and Dutta, 2010b). Sorption is more effective than precipitation at reducing F^- concentrations to 1 mg/L (Reardon and Wang, 2000) and is controlled by properties of the adsorbent and the physico-chemical conditions of the solution. It requires: 1) diffusion of F^- to the external surface of the adsorbent (i.e. mass transport); 2) adsorption onto the adsorbent surface; and 3) diffusion into the inner surfaces of the material (Fan, 2003). Studies have demonstrated the effectiveness of calcium carbonate materials, which are abundantly available in various forms such as lime or

---

* Corresponding author.
E-mail addresses: mhlecompte@gmail.com (M.H. Lecompte), brett.robinson@canterbury.ac.nz, brett.robinson@kiwiscience.com (B. Robinson), sally.gaw@canterbury.ac.nz (S. Gaw).
[1] Present address: Institute of Environmental Science and Research (ESR) 27 Creyke Road Ilam Canterbury 8041. New Zealand

https://doi.org/10.1016/j.clwat.2024.100025
Received 27 April 2024; Received in revised form 11 June 2024; Accepted 20 June 2024

hydroxyapatite, at F^- removal from drinking water (Vijayeeswarri et al., 2019). Though adsorption has advantages over other methods including effectiveness, low-cost, potential for reuse, availability of numerous adsorbents, and simple operation process and design (Mohapatra et al., 2009; Yadav et al., 2018; Kanaujia et al., 2015; Vinati et al., 2015), research is on-going as no material has been fully successful in resource constrained rural regions (Cherukumilli et al., 2018).

In calcite systems, both adsorption and precipitation occurs (Nath and Dutta, 2010a; Turner et al., 2005), which enables F^- removal in low concentrated solutions (Nath and Dutta, 2012), essential for generating safe drinking water. The reaction is heavily pH dependent (Yadav et al., 2018; Turner et al., 2005). Low pH in acid-enhanced lime defluoridation (AELD) increases calcium ion concentration in solution available for CaF precipitation (Nath and Dutta, 2010b; Gogoi and Dutta, 2016a) and protonates the adsorbent which increases its electrostatic attraction to F^- (Yadav et al., 2018). Edible acids (phosphoric, acetic and citric) are generally preferred and citric acid was used herein due to enhanced safety and accessibility.

Coral sand, a calcium carbonate material from coral reefs, is abundant between the latitudes of 30°N and 30°S and readily available in the Pacific Region where volcanic and geothermal activity are prevalent and consequentially, elevated F^- concentrations are common (Cronin et al., 2003; Allibone et al., 2012; Mallik, 1999). Given prior successes at F^- removal using limestone and the use of coral sand as a filtering medium for pathogen removal (Burbery et al., 2015; Humphries et al., 2016), we hypothesised that this material may also be a low-cost solution to remedy F^- contaminated drinking water. We aimed to utilise coral sand to develop low-cost water treatment devices to remove F^- from household drinking water. Specifically, we sought to determine: 1) the ability of coral sand to reduce F^- concentration in water using a filtration system, 2) the number of times the system could be reused before losing efficiency, and 3) the safety of treated water according to the World Health Organisation (World Health Organization, 2017) drinking water guidelines.

2. Materials and methods

2.1. Materials

Two grades of 'Natural Colour' coral sands (0.8–1.0 and 1–2 mm) were purchased from Living Reef (livingreef.co.nz). Coral sands were obtained from Bikenibeu beach, South Tarawa, Kiribati (1.367°N, 173.126° E) and Port Villa, Vanuatu (17.44°S, 168.18°E). Large particles were removed and the sand was oven dried at 60–65 °C for a minimum of 24 hours prior to use.

Plasticware was obtained from Stowers Containment Solutions (stower.co.nz). All chemicals used were analytical grade (≥ 99 % purity) with the exception of 'VALUE' brand food-grade citric acid purchased from a supermarket. Sodium fluoride (NaF) was oven dried at 60 °C for a minimum of 8 hours and stored in a dessicator until use. Solutions and reagents were made using ultrapure water (< 18.2 MΩ.cm).

Stock F^- solutions and calibration standards (0.25, 0.5, 2, 5, 10, 15 and 25 mg/L) were prepared gravimetrically. Laboratory control (LCS) and calibration curve verification (CCV) samples were prepared from a second batch of NaF. The Fluoride Standard for Ion Chromatography (1 g/L) was diluted to make spike solutions of 50, 100, 200, and 250 mg/L. Total ionic strength adjustment buffer (TISAB) was prepared from of 0.05 M disodium EDTA dihydrate, 1 M sodium chloride, 0.5 M glacial acetic acid and the pH was adjusted between 5 and 5.5 with NaOH.

2.2. Particle density and size distribution

The particle density of each sand type was determined according to the method described by Sarkar (Sarkar and Haldar, 2005). The particle size distribution (PSD) was determined by sieving according to the Wentworth (Wentworth, 1922) Scale classification and used to calculate mean particle size (refer supplementary data).

Table 1
Characteristics of the coral sands used in this study.

Characteristics (Average ± 2 SD)		Commercial Sands: Fine (0.8–1 mm)	Commercial Sands: Coarse (1–2 mm)	Pacific Beach Sands: Kiribati	Pacific Beach Sands: Vanuatu
Particle size distribution		Wentworth scale (% w/w) (Wentworth, 1922)			
Sieve Diameter (mm)	4+	—	—	* removed	* removed
	2	0 ± 0	0.04 ± 0.1	0.105	* removed
	1	25 ± 5	0.6 ± 0.2	76.9	7.53
	0.5	64 ± 2	47 ± 2	22.5	46.7
	0.25	10 ± 5	48 ± 2	0.488	35.1
	0.125	0.4 ± 0.3	4.1 ± 0.2	0.035	10.6
	0.063	0.07 ± 0.1	0.18 ± 0.03	0	0.059
	<0.063	0.02 ± 0.04	0.058 ± 0.003	0	0
Mean particle size (mm)		0.55 ± 0.01 (n=3)	0.90 ± 0.03 (n=3)	0.615 (n=1)	1.327 (n=1)
Particle density (g/cm^3, n=4)		2.82 ± 0.06	2.81 ± 0.02	2.78 ± 0.01	2.81 ± 0.03
Mineral composition Aragonite: Calcite (% weight)		72:28 ± 4	68:32 ± 4	44:56 ± 1	49:51 ± 8
Elemental composition (% weight)	O:	45 ± 2	Not done	46 ± 1	44 ± 10
	Ca:	32 ± 2		29 ± 2	26 ± 13
	C:	20 ± 1		22 ± 3	25 ± 10
	Mg:	1 ± 3		2 ± 3	1 ± 1

[*] Sand had been sieved prior to experimental trials. Mineral composition by X-ray Powder Diffraction, n=2 (n=4 for Vanuatu). Elemental composition by Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (n=3).

2.3. Scanning Electron Microscopy (SEM-EDX)

Triplicate samples of each sand type were carbon-coated using an EMS150T ES Quorum Carbon Coater and imaged (down to 1500 X) with backscatter and secondary electron detection using a JEOL JSM-IT300 EMS-SEM.

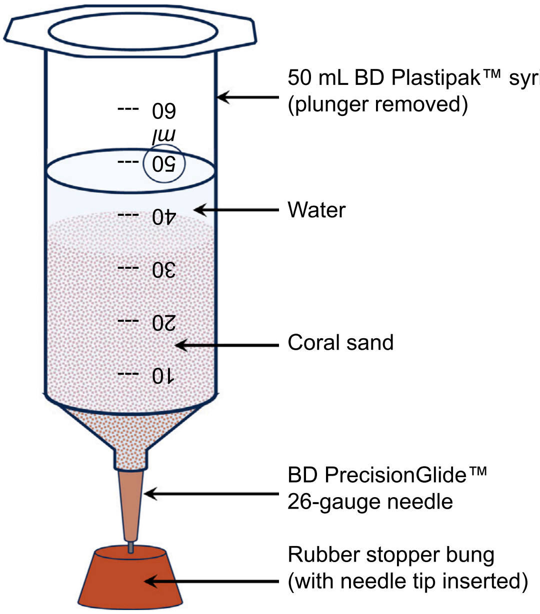


Fig. 1. Experimental mini column set-up. Syringe outer diameter of 29.4 mm and 133 mm length (Thermo Fisher Scientific, 2020).

2.4. X-ray diffraction (XRD)

Duplicate 1–2 g portions of dried untreated sand were ground using a mortar and pestle. Samples were mounted as a 0.5 mm layer on glass slides. Scans were made in 1D mode using a D-Tex detector from 5 – 65 ° at 5 °/min using a Cu Kβ filter and 5 ° soller slits. Data were processed on the Rigaku PDXL2 software, subtracting a polynomial background and calculating the relative amounts of phases using the RIR method. The ICDD (PDF4+ 2021) library was used for compound search.

2.5. Sand characterisation

The composition and particle size distribution of the sands used are listed in Table 1. SEM micrograms (refer Results) confirmed the high micro-porosity and surface area available for sorption of the coral sand, supporting its choice as a potentially good adsorbent.

2.6. Reactor preparation and experimental design

The experimental design conducted herein was in part modelled on published AELD studies conducted on limestone using various acids (Nath and Dutta, 2010a, 2010b, 2012; Gogoi and Dutta, 2016a). Preliminary trials conducted by the authors indicated high sand-to-fluid ratios were more effective at F^- removal as was moderate (0.025 or 0.050 M) citric acid concentrations and no remarkable improvements were noted by increasing contact time from four to eight hours (data not shown). An initial F^- concentration of 10 mg/L was selected as concentrations of F^- in drinking water sources in volcanic areas can exceed 4–5 mg/L (Rubio et al., 2020; Cordeiro et al., 2012).

Sand mini columns: The mini columns prepared from a Thermo Fisher Scientific 50 mL polypropylene syringe body and a 26-gauge needle were inserted into a rubber bung to impede fluid loss (Fig. 1). Initial solutions of 10.0 ± 0.2 mg/L (F^-) with 0.050 M or 0.025 M (± 4 %) citric acid were made daily, from a 1:1 dilution of stock 20.0 mg F^- /L solution and 0.10 M or 0.050 M citric acid, respectively. To test F^- removal, triplicate mini columns with 75 g of sand were filled with 25 mL of initial solution, equating to a sand-to-fluid ratio of 3:1. These were left to stand at room temperature for four hours prior to collecting the treated water. For subsequent refills, 15 mL of fluoride solution was added (5:1 ratio) to the top of the syringe as some water remained in the mini column. Mini columns were tested twice daily (morning and midday) to replicate use within a household, until F^- concentrations in the treated water exceeded 1.5 mg/L. A single, mini column with no sand was also processed with initial solution as a control.

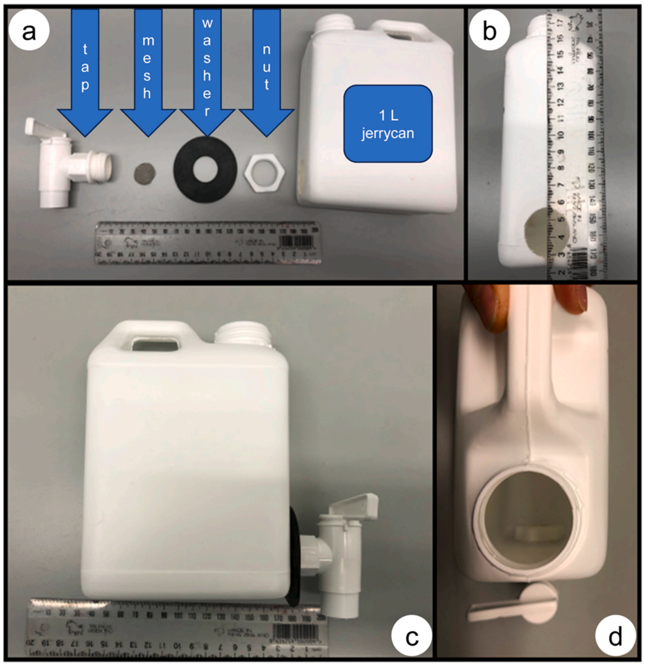


Fig. 2. Prototype assembly of 1 litre jerrycan with 1 kg of sand. A) parts disassembled; B) location and size of hand-made hole for tap; C) jerrycan assembled (side view); D) jerrycan assembled with no sand (top view). Outer measurements of the jerrycan are 123 mm deep x 67 mm wide x 168 mm high.

Prototypes with fine & coarse commercial sand: Pilot treatment devices were prepared from 1 L high density polyethylene jerrycan by inserting a ¾ inch BSP tap and back nut, through a hole approximately 0.7–1.0 cm from the bottom of the jerrycan (Fig. 2). Metal mesh of approximately 150–200 µm size was placed inside the tap and a 'Fix-a-loo' washer (fixatap.com.au) fitted to the exterior. Prototypes were thoroughly soaked and rinsed with dH_2O and ultrapure water prior to use. Triplicate prototypes containing 1000 g of commercial sand were loaded and emptied twice daily (morning and midday) with the same sand-to-fluid ratio as per the mini columns (i.e. 333.3 mL ± 0.5 % of initial solution containing 10.0 mg F^-/L and 0.025 M food-grade citric acid; 200 mL in subsequent fillings). The experiment was conducted with fine and coarse commercial sand. A single replicate with fine commercial sand was also processed as above using analytical grade citric acid (as opposed to food-grade). A single, no acid prototype was run alongside and a blank (no sand) prototype was also processed on day 1. Samples of the initial solutions were also analysed.

Sample collection and processing: Treated water was extracted by gravity by removing the needle assembly from mini columns or tilting prototypes at an angle of roughly 30 degrees into polystyrene 25 mL vials or 250 mL jars, respectively. The extracted treated water was homogenised and subsamples syringe-filtered (0.2 µm Ahlstrom Reliaprep™). Electrical conductivity of water treated with prototype devices was measured using a Hach HQ440d multimeter with a CDC401 conductivity probe and converted to estimated total dissolved solids (TDS) according to Eq. (1) (Taylor et al., 2018).

$$TDS = CF \times EC \tag{1}$$

Where,
EC = Electrical conductivity readings (µS/cm),
TDS = Total dissolved solids in mg/L,
CF = conversion factor (0.64) for high salinity samples (HACH, 2021).

2.7. FISE methodology and analysis

A calibration curve was prepared daily using standards diluted 1:1 with TISAB. The measured potential was entered into Excel to calculate the slope (S), intercept (E_0) and R value. Curves were deemed acceptable if: R Value ≥ 0.999; slope within −54 to −59; and standards within 10 % of prepared value.

For the filtered treated water samples, 2.5 mL was diluted 1:1 with TISAB and decomplexed for a minimum of 30 minutes. The pH was adjusted between 5.0 and 5.5 with 10 M NaOH as required and the electrode potential measured according to manufacturer recommendations (EDT, 2021) and ASTM standard (American Society for Testing and Materials International, 2016). Sample potential (E, in mV) was converted to F^- concentration in mg F^-/L based on the Nernst equation (International Organization for Standardization, 1992), according to Eq. (2):

$$[F^-] = 0.18998 \times 10^{(E-E0)/S} \tag{2}$$

Duplicates were ≤ 6 % different for F^- concentrations above 0.5 mg/L and ≤ 15 % for concentrations below 0.5 mg/L. Laboratory control samples were ≤ 15 % error. Ultrapure water was used as a reagent blank. A matrix spike and comparative standard (i.e. spiked reagent blank) was performed on one replicate per treatment type and the percent recovery (P) calculated according to Eq. 1 in the standard test method for fluoride (American Society for Testing and Materials International, 2016). The standardised percent recovery (P') of the spiked sample was calculated as per Eq. 3:

$$P' = 100\ x\ Psp / Pstn \tag{3}$$

Where,
$Pstn$ = Percent recovery of the comparative standard,
Psp = Percent recovery of the spiked sample.

To improve analytical results for samples where matrix interference was identified (i.e. P' outside the 80–120 % range), dilute FISE samples prepared from 1.25 mL treated water, 1.25 mL ultrapure water, and 2.5 mL TISAB were analysed as necessary (i.e. until P' of non-dilute FISE samples > 85 %). Additional details regarding the method performance is included in the supplementary data.

2.8. *Trace elements in treated water and coral sands*

Aliquots of filtered treated water were acidified with concentrated HNO_3 to pH <2 and refrigerated until analysis. Triplicate sand samples were acid digested in a microwave digestion system according to Method 3051 A (United States Environmental Protection Agency, 2007), along with two reagent blanks and a Certified Marine Sediment 2702 reference material (National Institute of Standards and Technology, 2019). The recoveries for trace elements were acceptable (refer Table 4). The treated water samples and sand digests were diluted with 2 % HNO_3 for trace element analysis (Al^{27}, $As^{75\ \&\ 75–91}$, B^{11}, Ca^{44}, Cr^{52}, Cu^{63}, $Fe^{56–72}$, Mg^{24}, Mn^{55}, Na^{23}, and Ni^{60}) by ICP-MS/MS (Agilent 8900) using He as a collision gas and O_2 as a reaction gas with Rh added online as an internal standard. Recoveries for relevant elements from the Trace Elements in Water Certified Reference Material (CRM) run daily measured between 85 – 115 % of reported values (National Institute of Standards and Technology, 2015). Trace element concentrations from initial solutions or blank columns/prototypes, whichever was highest, were deducted from the treated water samples concentrations and the control-deducted concentrations reported herein.

3. Results and discussion

SEM micrograms (example included in Fig. 3) did not reveal obvious differences in surface morphology before and after AELD treatment, nor between sand types which is in-line with findings from Nath et al. (Nath

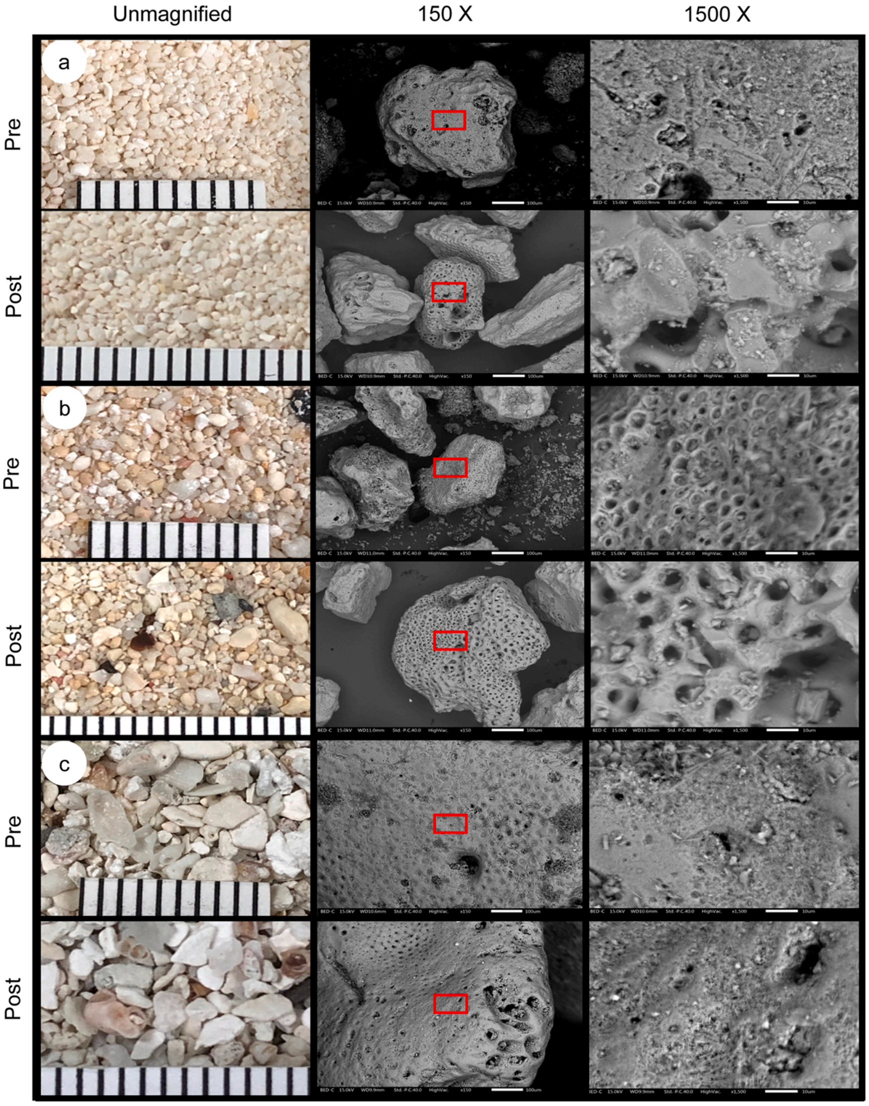


Fig. 3. General unmagnified and scanning electron microscopy (SEM) imaging of three coral sands, pre- and post- acid enhanced lime defluoridation: A) fine commercial, B) Kiribati, C) Vanuatu. Backspatter electron detection used at 150 X and 1500 X. White bars = 100 μm and 10 μm, respectively. Scale in unmagnified images in mm. Red box = magnified area at 1500 X.

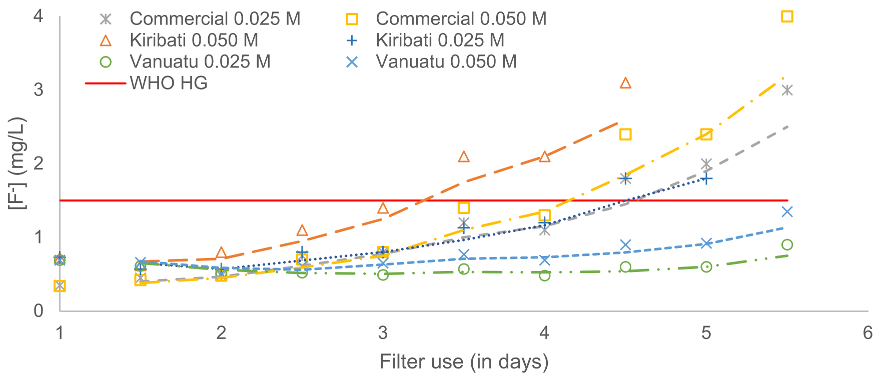


Fig. 4. Final F^- concentration of treated water vs. column use according to sand type and acid concentration used. Mini columns were used twice daily with 4-hour contact time. Average of n=3 (n=1 or n=2 on day 1, use 1); 2-per-moving-average trendline added. Errors omitted for clarity. Standardised percent recovery (P') of some treated water on days 1–3 were < 80 %. WHO HG drinking water guidelines for health (World Health Organization, 2017).

et al., 2011), who concluded that citric acid had no notable morphological effect on limestone, which suggests that coral sands could potentially be regenerated.

3.1. Sand mini column fluoride removal

The most likely fluoride removal mechanisms using calcium carbonate and acid are adsorption and precipitation, as previously documented (Nath and Dutta, 2010a; Turner et al., 2005; Nath and Dutta, 2012). Treatment with coral sand mini columns reduced the F^- concentration from 10 mg/L to below 1.5 mg/L over a period of 3.5–5 days (Fig. 4). These results are comparable to those of Nath and Dutta (Nath and Dutta, 2010a) who could reuse their reactor for an estimated nine days using 0.1 M citric acid and 12-hour contact.

Overall, the Vanuatu sand performed best, regardless of the citric acid concentration used. Mini columns could be reused for at least five days compared to 3 or 3.5 and 4 days using the Kiribati and finer commercial sand, respectively. This equates to approximately 90–105 mL of acidified water per 75 g of fine grained sands (0.55 and 0.62 mm) and a minimum of 150 mL with larger grained sand (1.33 mm). In essence, 0.01–0.02 mg of F^- was removed per g of sand before the treated water exceeded the 1.5 mg/L WHO drinking water guideline. The mineral composition of the sands is unlikely to have contributed to this enhanced F^- removal. The commercial sand had the lowest aragonite content of the three sands, ruling out that the enhanced F^- removal was due to a higher content of aragonite, which is more soluble than calcite (Stenzel, 1963) (refer Table 1).

3.1.1. Effect of particle size

There was an inverse relationship between particle size and F^- removal. It seems counterintuitive that larger particles (1.33 mm in Vanuatu sand) removed F^- better than smaller particles (0.55 and 0.62 mm for fine commercial and Kiribati sands) since larger particles have lower surface area (Mavura et al., 2004). Most authors have reported no appreciable difference or increased F^- removal with smaller particles (Nath and Dutta, 2010a; Mondal et al., 2016; Wong and Stenstrom, 2018). Particle size does, however, affect pore volume. It is hypothesised that Vanuatu mini columns could be reused more often because the larger particles resulted in more sand volume and pore space, leaving a lower head-volume of water in the columns. As headwater is not in close contact with the absorbent, it remained effectively untreated and would contain F^- at or near the initial concentration of 10.0 mg/L. Finer sand mini columns contained more of this headwater, accounting for the higher F^- concentration of the resultant treated water.

3.1.2. Effect of citric acid concentration on fluoride removal

Reducing the acid strength from 0.050 M to 0.025 M (or 0.15 N to 0.075 N given citric acid is triprotic) improved F^- removal, though not substantially so for all sands as the 2-standard error overlapped (Fig. 4 – error not shown). This contradicts findings from published AELD studies using oxalic, acetic or citric acids, whereby increasing acid concentration enhanced F^- removal (Nath and Dutta, 2010b, 2012). These results may be due to the pre-existing F^- content of coral sand. Preliminary matrix recovery experiments (refer supplementary data) indicated F^- was present in the coral sand naturally, and desorbed into solutions of low or zero F^- concentration. In contrast, limestone used by other researchers did not appear to contain appreciable concentrations of F^-

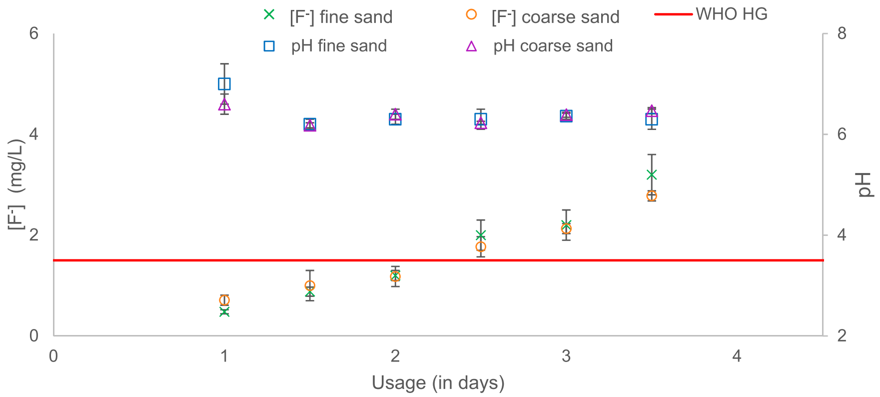


Fig. 5. Comparison of final F^- concentration and pH of treated water following repeated use of fine vs. coarse sand prototypes. Initial solution of 10 mg F^-/L and 0.025 M food grade citric acid used twice daily with 5:1 sand-fluid ratio. Average ± 2 SD (n=3, n=2 fine sand on day 3.5). WHO HG drinking water guidelines for health (World Health Organization, 2017).

(Turner et al., 2005; Labastida et al., 2017). The addition of acid to the calcite carbonate sand produced CO_2 gas. It was noted that increasing the acid altered the volume of water able to be extracted as well as the sand packing of the mini columns thereby increasing the pore volume and lowering the head volume. This was only noted in hindsight and not specifically quantified throughout the study. The additional extracted volume resided in the head-volume where little to no F^- removal could occur, thus an increase in total volume extracted was observed to be related to a higher final F^- concentration of treated water.

3.2. Fluoride removal in prototype treatment system

Results from the sand prototype experiment with 0.025 M food grade acid are summarised in Fig. 5. The prototypes containing fine (0.55 mm) coral sand could only reduce F^- to below 1.5 mg/L for three uses, which equates to approximately 600 mL of treated water per kg of sand. Unlike with the mini columns, increasing the particle size did not increase F^- removal. The particle size increase in prototypes (0.55 mm to 0.90 mm) was not as large as in the mini columns (0.61 mm to 1.32 mm) and may not have been sufficient to create a measurable effect in F^- removal. As expected, the pH in fine vs. coarse sand treated water was similar and not an indication of concern. The same batch of analytical grade (AR) acid used in the mini columns was used in a prototype, resulting in only slightly lower final F^- concentrations. This prototype could also only be used three times to reduce F^- below 1.5 mg/L (data not shown), indicating the difference in performance between mini columns and prototypes is unlikely due to different grade or batch of acid.

The prototypes were only able to lower F^- below 1.5 mg/L for a maximum of three uses compared with a minimum of seven for the mini columns, regardless of particle size (using the same experimental protocols). The observed difference in removal of F^- may be due to the shape of the different treatment systems altering processes such as fluid mechanics, retention, preferential flow, sand compaction, and/or capillary forces. It was observed that, mini columns generally retained slightly more fluid than the prototypes, enabling a longer contact time with the absorbent which would enhance F^- removal in subsequent filter uses. Higher efficiency of fluoride removal in columns compared to bucket filters has been previously noted for bone charcoal filters (Fawell et al., 2006). Filter shape appears critical in enhancing F^- removal with coral sand, and future design may benefit from two successive filters or more elongated dimensions.

3.3. Comparison of treated water to drinking water guidelines

Trace element concentrations in water treated with mini sand columns (refer Table 2) exceeded WHO (World Health Organization, 2017) drinking water guidelines for health (As, B, Cr, Mn, Ni) and aesthetic acceptability (Al, Ca, Fe, Mg, Mn, Na and hardness as determined from the concentration of Mg and Ca). Generally, trace element concentrations in the treated water decreased with usage, with the highest concentrations measured during the first 1–3 uses of the mini column (Table 2 and Fig. 6). For most trace elements, higher concentrations were measured in the beach sand-treated water, particularly with sand which had been reused less often, compared with the commercial sand (Fig. 6 and Table 2).

The number of consecutive days the treated water exceeded the WHO guidelines varied between trace elements from 1 to 5 days. Chromium concentrations were of most concern, as the WHO health guideline was exceeded for all sand types and over the duration of the up-to 5-day trial. Similarly, As was persistently above guidelines in water treated with the beach sands, particularly so for the Kiribati sand, but only exceeded the guideline in commercial sand for 2–3 days. Nickel exceeded health guidelines for the first day of usage with beach sands only. Manganese was above the health guideline in the water treated with 0.050 M acid and Vanuatu sand on day 1 only, and above aesthetic acceptability for all sands throughout the trial (Fig. 6). Sodium and B were above WHO aesthetic and health guideline, respectively, in beach sand-treated water during the first 2–3 days of usage. Increasing acid concentration, for the most part, increased trace elements released, most likely as a results of sand dissolution (Table 2). The persistent presence of elevated Al and Fe concentrations in all treated water explain the matrix interference issues encountered as both elements are well-documented electrode interferents, as are B and OH^- (American Society for Testing and Materials International, 2016; Baird and Bridgewater, 2017; EDT DirectION, 2021). The presence of Ca above guideline is expected as acid reacts with sand releasing the ion. All treated water samples also exceeded WHO aesthetic acceptability with regards to hardness and total dissolved solids.

Fewer elements of health and aesthetic concern exceeded WHO drinking water guidelines in prototype treated water (Table 3). Aluminium, Ca, Cr, Fe, Mg, and Mn exceeded guidelines for all water samples where F^- was lowered from 10 to below 1.5 mg/L (up to 1.5 days or 3 uses) with fine or coarse sand and 0.025 M acid. Though As exceeded health guideline for all tested water samples treated with fine sand and 0.025 M acid, values remained below guideline after day 1 of treatment with coarse sand. Analysis of the initial solutions and 'no sand' controls confirmed that the F^- and citric acid were not a source of the trace elements. Our findings for trace elements contradict other AELD studies performed with limestone and oxalic or citric acid where trace elements were not of concern (Nath and Dutta, 2010a, 2012).

Of those above WHO health guidelines, As is the element of most concern in natural water sources and a documented carcinogen (World

Table 2
Trace elements above WHO (World Health Organization, 2017) health guideline (HG) and aesthetic acceptability (AA) in treated water following repeated use of mini columns prepared from three sand types with 0.025 or 0.050 M citric acid.

Element	Guidelines		Units	LOQ	Commercial (fine) Sand		Kiribati Sand		Vanuatu	
	HG	***AA***			0.025 M	0.050 M	0.025 M	0.050 M	0.025 M	0.050 M
As	10		μg/L	2.9	Day 1–2 (31)	Day 1–3 (39)	All (570)	All (640)	All (99)	All (110)
B	2.4		mg/L	0.21	—	—	Day 1–2 (6.5)	Day 1–2 (7.1)	Day 1–3 (8.4)	Day 1–3 (9.8)
Cr	50		μg/L	29	All (160)	All (250)	All (190*)	All (250)	All (540)	All (930)
Ni	70		μg/L	2.9	—	—	Day 1 (170)	Day 1 (180)	Day 1 (92)	Day 1 (140)
Al		0.1–0.2	mg/L	0.29	All (2.4)	All (2.4)	All (1.3)	All (1.3)	All (2.5)	All (3.2)
Ca		100–500	mg/L	21	All (1400)	All (1600)	All (1500*)	All (2200)	All (1300)	All (2400)
Fe		0.3	mg/L	0.21	All (1.9)	All (2.3)	All (6.2*)	All (6.7)	All (2.5)	All (3.4)
Mg		100–500	mg/L	21	All (140)	All (210)	All (670)	All (730)	All (780)	All (830)
Mn	400	100	μg/L	29	All (150)	All (240)	All (180*)	All (260)	All (280)	All** (490)
Na		200	mg/L	2.1	—	—	Day 1–2 (3300)	Day 1–2 (3000)	Day 1–3 (7800)	Day 1–3 (7000)
Hardness		100–500	mg/L	42	All (1500)	All (1800)	All (1800)	All (3000)	All (2000)	All (3100)

Number of days where treated water samples were above limit is listed (mini columns used twice daily with an initial solution of 10 mg F^-/L). All = all sampled tested (where $[F^-]$/L was below 1.5 mg/L). Bracketed number is highest average value (n=2, *n=1) with control deducted. **Mn above WHO HG on day 1, and above AA for remainder of experiment. Hardness calculated from [Ca] + [Mg]. LOQ = Limit of Quantitation

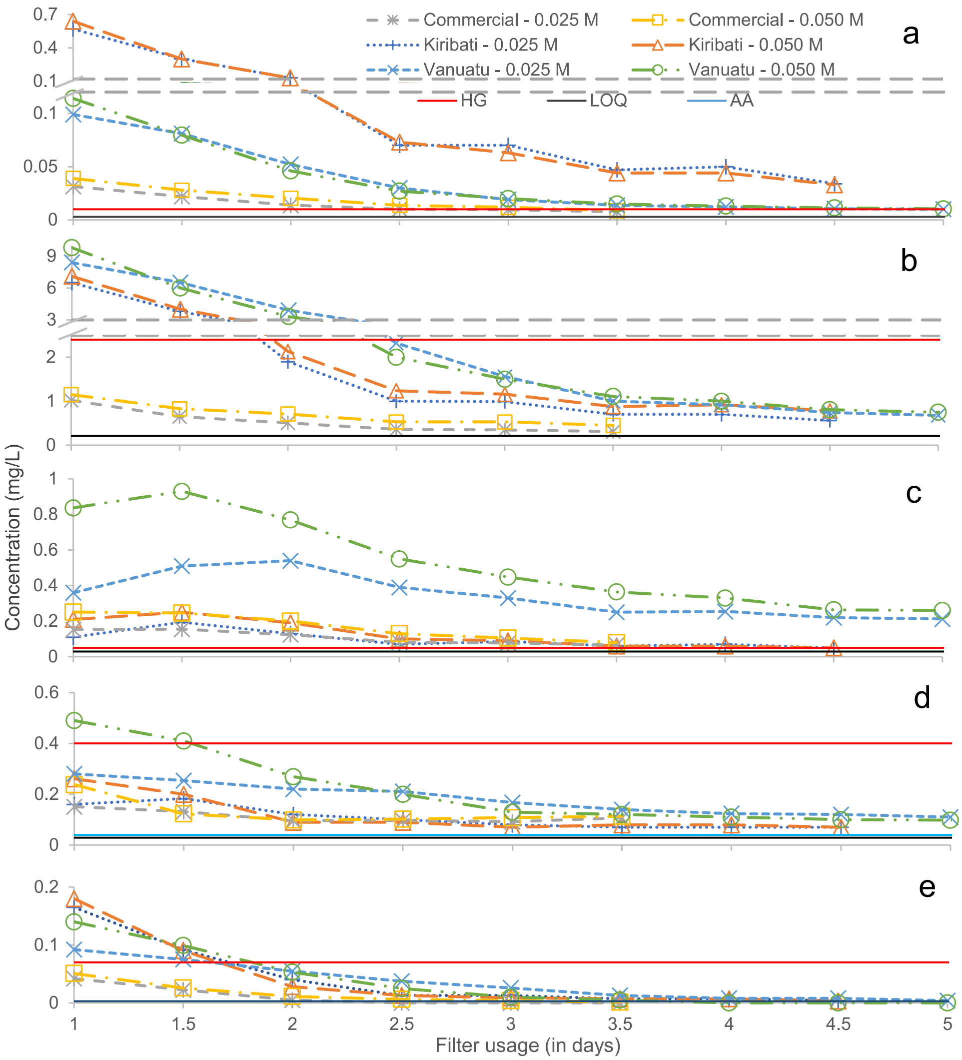


Fig. 6. Concentration of trace elements above WHO (World Health Organization, 2017) drinking water guidelines in treated water vs. repeated column use using 0.025 or 0.050 M citric acid: a) Arsenic, b) Boron, c) Chromium, d) Manganese and e) Nickel. Initial solution of 10 mg F⁻/L treated with mini columns prepared from varied sand types using a 5:1 sand-to-fluid ratio, mini columns used twice daily. LOQ = Limit of Quantitation. AA = aesthetic acceptability. HG = health guideline.

Table 3
Trace elements above WHO (World Health Organization, 2017) health guideline (HG) and aesthetic acceptability (AA) in sand treated water following repeated use of prototypes (fine or coarse commercial sand) with 0.025 M citric acid.

Element	Guidelines		Units	LOQ	Fine Sand		Coarse Sand	
	HG	*AA*			0 M	0.025 M	0 M	0.025 M
As	10		μg/L	2.1	—	All (23)	—	Day 1 (12)
Cr	50		μg/L	2.1	—	All (128)	Use 1 (85)	All (130)
Al		100–200	μg/L	210	—	All (1700)	Day 1 (1300)	All (1700)
Ca		100–500	mg/L	212	—	All (1600)	—	All (1700)
Fe		300	μg/L	21	—	All (1300)	Use 1 (900)	All (1200)
Mg		100–500	mg/L	2.1	—	All (110)	—	All (120)
Mn	400	100	μg/L	21	—	All (120)	—	All (100)
Hardness		100–500	mg/L	215	—	All (4500)	—	All (5000)
TDS		1	g/L		—	All (1.5)	—	All (1.5)

Initial solution of 10 mg F⁻/L treated with 5:1 sand-fluid ratio prototypes, used twice daily. Number of days above limit is listed. All = all sampled tested which included up to Day 2, use 1. Number in brackets is highest average value measured (n=3, n=1 for 0 M), with control deducted. Hardness calculated from [Ca] + [Mg]. TDS = total dissolved solids. LOQ = Limit of Quantitation.

Health Organization, 2017). Consumption of As-contaminated waters has been associated with various health issues including: peripheral vascular disease and neuropathy; skin lesions; bladder, lung, and skin cancers; problematic child and foetal developmental (World Health Organization, 2017; Vahter et al., 2020), to name a few. Though Cr (III) is an essential element with no apparent adverse long-term effects through oral consumption (World Health Organization, 2020), Cr (VI) is carcinogenic (World Health Organization, 2020; Georgaki et al., 2023) and has been associated with various human respiratory, immune, reproductive, digestive and GI dysfunctions (Georgaki and

Table 4
Trace element concentrations in the sands used to make the mini columns and prototype treatment devices.

Element	Elemental Composition (in mg/kg)				LOQ	SRM % Recovery
	Vanuatu	Kiribati	Commercial (fine)	Commercial (coarse)		
Al	800 ± 1300	60 ± 20	150 ± 10	100 ± 20	3.5	88
As	2.5 ± 0.7	3 ± 1	1.6 ± 0.2	1.9 ± 0.2	0.35	77
B	50 ± 8	76 ± 8	71 ± 9	58 ± 6	3.5	n/a
Cd	<LOQ	0.084 ± 0.008	<LOQ	0.05 ± 0.01	0.035	93
Co	0.1 ± 0.1	0.2 ± 0.4	0.044 ± 0.008	<LOQ	0.035	87
Cr	8 ± 5	3 ± 3	2.1 ± 0.3	2.3 ± 0.4	0.035	80
Cu	0.67 ± 0.07	3 ± 5	0.21 ± 0.07	0.14 ± 0.01	0.035	87
Fe	200 ± 300	6000 ± 12000	120 ± 80	30 ± 10	0.35	68
Mn	10 ± 4	30 ± 30	9 ± 2	11 ± 4	3.5	96
Ni	0.4 ± 0.2	1 ± 2	0.38 ± 0.04	0.29 ± 0.04	0.035	84
Pb	1.9 ± 0.3	40 ± 110	0.4 ± 0.07	0.4 ± 0.06	0.035	85
Zn	1.3 ± 0.9	7.2 ± 2.	1.4 ± 0.4	1.5 ± 0.4	0.35	120
	Elemental Composition (in g/kg)					
Ca	340 ± 20	330 ± 40	330 ± 40	330 ± 20	0.035	73
Mg	14 ± 4	17 ± 2	6.3 ± 0.6	9 ± 4	0.0035	88
Na	4.4 ± 0.5	4.3 ± 0.2	3.4 ± 0.1	3.1 ± 0.2	0.00035	72
S	1.6 ± 0.3	1.7 ± 0.3	1.4 ± 0.1	1.4 ± 0.3	0.035	62

Average ± 2 SD (n=3) with average of two blanks deducted. LOQ = Limit of Quantitation; SRM = Standard Reference Material (National Institute of Standards and Technology, 2019).

Charalambous, 2023; Pellerin and Booker, 2000).

3.4. Trace elements in coral sands

Analysis of the sand for trace elements confirmed the presence of electrode interferents (Al, B, and Fe) and elements of health and aesthetic concern (notably Al, As, Cr, Fe, Mn, and Ni) (Table 4). The most likely source of these trace elements is the geographical origins of the sands. Arsenic is prevalent in regions with volcanic and hydrothermal activity (Bundschuh et al., 2010; Masuda, 2018). Additionally, Ambae (Vanuatu) lava contains a notable amount of Cr (500–1600 mg/kg), Mn (1100–1200 mg/kg), and Ni (100 – 600 mg/kg) (Park et al., 2012). This presence of trace elements has implications for the use of coral sand in drinking water treatment. Firstly, additional treatment would be required to reduce trace elements from treated water to acceptable concentrations. Potential options for remediation of elevated As and Cr could include sorption on bioadsorbents, activated carbon, metal oxide coated on sands, zero-valent iron (Chowdhury, 2012; Cornejo et al., 2008; Garcia Ferreira et al., 2023; Rahidul Hassan, 2023; Chen et al., 2018), to name a few. Activated carbon could potentially resolve any aesthetic issues as well (Chowdhury, 2012). Pre-treating the sand to flush out trace contaminants present prior to defluoridation is a potential alternative. Secondly, water quality monitoring following coral sand treatment is advisable and could be as simple as employing commercially available test strips for arsenic (camlab.co.uk; coleparmer.com) and drinking water test kits (amazon.com; alibaba.com).

3.5. Cost-effectiveness, defluoridation capacity and reuse of the limestone

The proposed method is low-cost and hence potentially suitable in resource constrained settings. As sand may be collected from coral beaches and no power is required for treatment, the ongoing cost of fluoride removal is governed by the local price of citric acid. Using 0.025 M acid (4.8 g/L), and assuming an inflated purchased price of 5 $/kg, treatment costs less than 0.025 $/L. This estimate does not factor in pre- or post-treatment to remedy elevated trace contaminants.

Though not undertaken in this study, regeneration of the coral sands could be attempted with scrubbing or soaking in alkaline solution (El Messaoudi et al., 2024; Gogoi et al., 2015; Nath and Dutta, 2010a). Care would need to be taken with regeneration of sands as it could further mobilise trace elements. Given ease of access, replacement as opposed to regeneration of sand may be simpler. The environmental impact of returning the F^- saturated coral sand into the sea would be negligeable given the high geogenic levels of F^- in the tropical region and the excessive volume of sea water.

The operational defluoridation capacity of the coral sands using 0.025 M citric acid, to decreased F^- concentration from 10 mg/L to below 1.5 mg/L in mini columns of fine and coarse sands was estimated to be 1.4 L/kg and >2 L/kg respectively, whereas the prototypes capacity was limited to 0.6 L/kg of sand, regardless of particle size. This equates to 0.011–0.020 mg/g in mini columns vs. 0.007 mg/g in prototypes. Various treatments applied to adsorbents (e.g. thermal, chemical coating) (Gogoi and Dutta, 2016b; Lee et al., 2021; Chang et al., 2019; He et al., 2020) have significantly enhanced their adsorption capacity and could be explored with coral sands.

4. Conclusions

AELD treatment with coral sands reduced 10 mg/L fluoride solution to below the WHO 1.5 mg/L limit for drinking water, with mini columns more successful than 1 L polyethylene prototypes. In mini columns, approximately 100 mL of acidified water could be treated with 75 g of fine grained sands (0.55 and 0.62 mm) and a minimum of 150 mL could be treated with larger grained sand (1.33 mm). One kg of fine sand (0.55 and 0.90 mm) in 1 L prototype devices could only successfully reduce fluoride below 1.5 mg/L in approximately 600 mL of acidified water. Key findings of this study are that a 'goldilocks' range of particle size exists and filter shape are significant factors in optimizing F^- removal. Determining this range and optimising filter design should be the focus of future research. Due to the presence of trace elements in the sands, trace element concentrations in the treated water exceeded WHO drinking water guidelines for human health (As, B, Cr, Ni, Mn) and aesthetic acceptability (Al, Ca, Fe, Mg, Mn, Na). Further work is required to include a second treatment stage to remove trace elements from water or remove trace metal contaminants from coral sand prior to use as a water filtering medium.

CRediT authorship contribution statement

MH Lecompte: Writing – original draft, Visualization, Project administration, Investigation, Funding acquisition, Formal analysis. B. Robinson: Writing – review & editing, Supervision, Methodology. S. Gaw: Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used in this manuscript is available in the corresponding author's Master's thesis, available from the UC (University of Canterbury) Research Repository.

Acknowledgement

The authors thank University of Canterbury staff and students for technical assistance (Dr M. Polson, Dr N. Alexander, C. Grimshaw, R. Stainthorpe, N. Oliver and H. Thompson-Morrison); colleagues at ESR for procurement of coral sand and/or constructive feedback (M. Ashworth, Dr L. Weaver, Dr J. Gregor, Dr L. Burbery, B. Humphries). This work was supported by a scholarship from the Waterways Centre for Freshwater Management, University of Canterbury.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.clwat.2024.100025.

References

Alarcón-Herrera, M.T., Bundschuh, J., Nath, B., Nicolli, H.B., Gutierrez, M., Reyes-Gomez, V.M., Nuñez, D., Martín-Dominguez, I.R., Sracek, O., 2013. Co-occurrence of arsenic and fluoride in groundwater of semi-arid regions in Latin America: Genesis, mobility and remediation. J. Hazard. Mater. 262, 960–969. https://doi.org/10.1016/j.jhazmat.2012.08.005.

Allibone, R., Cronin, S.J., Charley, D.T., Neall, V.E., Stewart, R.B., Oppenheimer, C., 2012. Dental fluorosis linked to degassing of Ambrym volcano, Vanuatu: A novel exposure pathway. Environ. Geochem. Health 34, 155–170. https://doi.org/10.1007/s10653-010-9338-2.

American Society for Testing and Materials International, Standard Test Methods for Fluoride Ion in Water, (2016). ASTM. D1179-16.

Ayoob, S., Gupta, A.K., 2006. Fluoride in drinking water: A review on the status and stress effects. Crit. Rev. Environ. Sci. Technol. 36, 433–487. https://doi.org/10.1080/10643380600678112.

Baird, R., Bridgewater, L. (Eds.), 2017. Standard Methods for the Examination of Water and Wastewater, 23rd edition. American Public Health Association, Washington, D.C.

Bundschuh, J., Litter, M., Ciminelli, V.S.T., Morgada, M.E., Cornejo, L., Hoyos, S.G., Hoinkis, J., Alarcón-Herrera, Ma.T., Armienta, M.A., Bhattacharya, P., 2010. Emerging mitigation needs and sustainable options for solving the arsenic problems of rural and isolated urban areas in Latin America – A critical analysis. Water Res 44, 5828–5845. https://doi.org/10.1016/j.watres.2010.04.001.

Burbery, L., Weaver, L., Humphries, B., Gregor, J., 2015. Efficacy of coral sand for removal of *Escherichia coli* and bacteriophage under saturated flow conditions. J. Environ. Qual. 44, 1384–1391. https://doi.org/10.2134/jeq2015.01.0044.

Chang, H.Y.H., Kuo, Y.-L., Liu, J.C., 2019. Fluoride at waste oyster shell surfaces – Role of magnesium. Sci. Total Environ. 652, 1331–1338. https://doi.org/10.1016/j.scitotenv.2018.10.238.

Chen, Y., An, D., Sun, S., Gao, J., Qian, L., 2018. Reduction and removal of chromium VI in water by powdered activated carbon. Materials 11, 269. https://doi.org/10.3390/ma11020269.

Cherukumilli, K., Maurer, T., Hohman, J.N., Mehta, Y., Gadgil, A.J., 2018. Effective remediation of groundwater fluoride with inexpensively processed Indian bauxite. Environ. Sci. Technol. 52, 4711–4718. https://doi.org/10.1021/acs.est.7b05539.

Chowdhury, Z., 2012. Activated Carbon: Solutions for Improving Water Quality, Illustrated edition. American Water Works Assn, Denver.

Cordeiro, S., Coutinho, R., Cruz, J.V., 2012. Fluoride content in drinking water supply in São Miguel volcanic island (Azores, Portugal). Sci. Total Environ. 432, 23–36. https://doi.org/10.1016/j.scitotenv.2012.05.070.

Cornejo, L., Lienqueo, H., Arenas, M., Acarapi, J., Contreras, D., Yáñez, J., Mansilla, H.D., 2008. In field arsenic removal from natural water by zero-valent iron assisted by solar radiation. Environ. Pollut. 156, 827–831. https://doi.org/10.1016/j.envpol.2008.05.022.

Cronin, S.J., Neall, V.E., Lecointre, J.A., Hedley, M.J., Loganathan, P., 2003. Environmental hazards of fluoride in volcanic ash: a case study from Ruapehu volcano, New Zealand. J. Volcanol. Geotherm. Res. 121, 271–291. https://doi.org/10.1016/S0377-0273(02)00465-1.

D'Alessandro, W., 2006. Human fluorosis related to volcanic activity: A review. In: Environ. Toxicol. WIT Press, Mykonos, Greece, pp. 21–30. https://doi.org/10.2495/ETOX060031.

EDT DirectION, Combination ISE range. EDT DirectION electrochemistry products, n.d. https://www.edt.co.uk/Fluoride-Combination-Ion-Selective-Electrode (accessed June 6, 2021).

EDT DirectION, Fluoride ISE – 3221 [Instruction Manual]. EDT DirectION electrochemistry products, n.d. https://www.edt.co.uk/Fluoride-Combination-Ion-Selective-Electrode (accessed June 6, 2021).

Fan, X., 2003. Adsorption kinetics of fluoride on low cost materials. Water Res 37, 4929–4937. https://doi.org/10.1016/j.watres.2003.08.014.

Fawell, J., Bailey, K., Chilton, J., Dahi, E., Fewtrell, L., Magara, Y., 2006. Fluoride in Drinking-Water. World Health Organization. 〈https://iris.who.int/handle/10665/43514〉.

Garcia Ferreira Jr, J.E., Maia, L.C., dos Santos, G.R., Soares, L.C., Gurgel, L.V.A., 2023. An affordable bioadsorbent system to treat arsenic-contaminated drinking water in the developing world: Prototyping and economic assessment. J. Environ. Chem. Eng. 11, 111199 https://doi.org/10.1016/j.jece.2023.111199.

Georgaki, M.-N., Charalambous, M., Kazakis, N., Talias, M.A., Georgakis, C., Papamitsou, T., Mytiglaki, C., 2023. Chromium in water and carcinogenic human health risk. Environments 10, 33. https://doi.org/10.3390/environments10020033.

Georgaki, M.-N., Charalambous, M., 2023. Toxic chromium in water and the effects on the human body: a systematic review. J. Water Health 21, 205–223. https://doi.org/10.2166/wh.2022.214.

Gogoi, S., Nath, S.K., Bordoloi, S., Dutta, R.K., 2015. Fluoride removal from groundwater by limestone treatment in presence of phosphoric acid. J. Environ. Manag. 152, 132–139. https://doi.org/10.1016/j.jenvman.2015.01.031.

Gogoi, S., Dutta, R.K., 2016a. Mechanism of fluoride removal by phosphoric acid-enhanced limestone: equilibrium and kinetics of fluoride sorption. Desalin. Water Treat. https://doi.org/10.1080/19443994.2015.1010592.

Gogoi, S., Dutta, R.K., 2016b. Fluoride removal by hydrothermally modified limestone powder using phosphoric acid. J. Environ. Chem. Eng. 4, 1040–1049. https://doi.org/10.1016/j.jece.2016.01.004.

HACH, Conductivity and total dissolved solids, n.d. https://www.hach.com/asset-get.download.jsa?id=10929896653 (accessed June 6, 2021).

He, J., Yang, Y., Wu, Z., Xie, C., Zhang, K., Kong, L., Liu, J., 2020. Review of fluoride removal from water environment by adsorption. J. Environ. Chem. Eng. 8, 104516 https://doi.org/10.1016/j.jece.2020.104516.

B.L. Humphries, L. Weaver, L.F. Burbery, J. Gregor, Coral beach sand as engineered sand filter in septic tank effluent drainage fields in Kiribati, in: Rotorua, 2016.

International Organization for Standardization, Water Quality - Determination of Fluoride - Part 1: Electrochemical Probe Method for Potable and Lightly Polluted Water, (1992). ISO. 10359-1:1992(E).

Kanaujia, S., Singh, B., Singh, S.K., 2015. Removal of fluoride from groundwater by pcarbonised Punica granatum carbon ("CPGC") bio-adsorbent. J. Geosci. Environ. Prot. 03, 1–9. https://doi.org/10.4236/gep.2015.34001.

Keesari, T., Sinha, U.K., Kamaraj, P., Sharma, D.A., 2019. Groundwater quality in a semi-arid region of India: Suitability for drinking, agriculture and fluoride exposure risk. J. Earth Syst. Sci. 128, 24. https://doi.org/10.1007/s12040-018-1049-6.

Kimambo, V., Bhattacharya, P., Mtalo, F., Mtamba, J., Ahmad, A., 2019. Fluoride occurrence in groundwater systems at global scale and status of defluoridation – State of the art. Groundw. Sustain. Dev. 9, 100223 https://doi.org/10.1016/j.gsd.2019.100223.

Labastida, I., Armienta, M.A., Beltrán, M., Caballero, G., Romero, P., Rosales, M.A., 2017. Limestone as a sustainable remediation option for water contaminated with fluoride. J. Geochem. Explor. 183, 206–213. https://doi.org/10.1016/j.gexplo.2016.12.001.

Lee, J.-I., Kang, J.-K., Hong, S.-H., Lee, C.-G., Jeong, S., Park, S.-J., 2021. Thermally treated *Mytilus coruscus* shells for fluoride removal and their adsorption mechanism. Chemosphere 263, 128328. https://doi.org/10.1016/j.chemosphere.2020.128328.

Levy, S., 2005. Total fluoride intake higher in subjects of low socioeconomic status. J. Evid. Based Dent. Pract. 5, 209–210. https://doi.org/10.1016/j.jebdp.2005.09.014.

Mallik, T.K., 1999. Calcareous sands from a coral atoll-should it be mined or not? Mar. Georesources Geotechnol. 17, 27–32. https://doi.org/10.1080/106411999273981.

Masuda, H., 2018. Arsenic cycling in the Earth's crust and hydrosphere: Interaction between naturally occurring arsenic and human activities. Prog. Earth Planet. Sci. 5, 68. https://doi.org/10.1186/s40645-018-0224-3.

Mavura, W.J., Mwanyika, F.T., Wrensford, G., 2004. Construction and optimisation of a cartridge filter for removing fluoride in drinking water. Bull. Chem. Soc. Ethiop. 18 https://doi.org/10.4314/bcse.v18i1.61630.

Meenakshi, Maheshwari, R.C., 2006. Fluoride in drinking water and its removal. J. Hazard. Mater. 137, 456–463. https://doi.org/10.1016/j.jhazmat.2006.02.024.

El Messaoudi, N., Franco, D.S.P., Gubernat, S., Georgin, J., Şenol, Z.M., Ciğeroğlu, Z., Allouss, D., El Hajam, M., 2024. Advances and future perspectives of water defluoridation by adsorption technology: A review. Environ. Res. 252, 118857 https://doi.org/10.1016/j.envres.2024.118857.

Mohapatra, M., Anand, S., Mishra, B.K., Giles, D.E., Singh, P., 2009. Review of fluoride removal from drinking water. J. Environ. Manag. 91, 67–77. https://doi.org/10.1016/j.jenvman.2009.08.015.

Mondal, N.K., Bhaumik, R., Datta, J.K., 2016. Fluoride adsorption by calcium carbonate, activated alumina and activated sugarcane ash. Environ. Process. 3, 195–216. https://doi.org/10.1007/s40710-016-0130-x.

Nath, S.K., Bordoloi, S., Dutta, R.K., 2011. Effect of acid on morphology of calcite during acid enhanced defluoridation. J. Fluor. Chem. 132, 19–26. https://doi.org/10.1016/j.jfluchem.2010.10.007.

Nath, S.K., Dutta, R.K., 2010a. Enhancement of limestone defluoridation of water by acetic and citric acids in fixed bed reactor. CLEAN – Soil Air Water 38, 614–622. https://doi.org/10.1002/clen.200900209.

Nath, S.K., Dutta, R.K., 2010b. Fluoride removal from water using crushed limestone. Indian J. Chem. Technol. 17, 120–125.

Nath, S.K., Dutta, R.K., 2012. Acid-enhanced limestone defluoridation in column reactor using oxalic acid. Process Saf. Environ. Prot. 90, 65–75. https://doi.org/10.1016/j.psep.2011.07.001.

National Institute of Standards and Technology, 2019. Certificate of Analysis - Standard Reference Material 2702 - Inorganics in Marine Sediment. NIST. SRM 2702. https://www-s.nist.gov/m-srmors/certificates/2702.pdf.

National Institute of Standards and Technology, 2015. Certificate of Analysis - Trace Elements in Water. NIST. SRM 1643f:2015. https://www-s.nist.gov/m-srmors/view_certPDF.cfm?certificate=1643f.

Park, J.-W., Campbell, I.H., Eggins, S.M., 2012. Enrichment of Rh, Ru, Ir and Os in Cr spinels from oxidized magmas: Evidence from the Ambae volcano, Vanuatu. Geochim. Cosmochim. Acta 78, 28–50. https://doi.org/10.1016/j.gca.2011.11.018.

Pellerin, C., Booker, S.M., 2000. Reflections of hexavalent chromium: health hazards of an industrial heavyweight. Environ. Health Perspect. 108, A402–A407. https://doi.org/10.1289/ehp.108-a402.

Rahidul Hassan, H.A., 2023. A review on different arsenic removal techniques used for decontamination of drinking water. Environ. Pollut. Bioavailab. 35 https://doi.org/10.1080/26395940.2023.2165964.

Reardon, E.J., Wang, Y., 2000. A limestone reactor for fluoride removal from wastewaters. Environ. Sci. Technol. 34, 3247–3253. https://doi.org/10.1021/es990542k.

Rubio, C., Rodríguez, I., Jaudenes, J.R., Gutiérrez, A.J., Paz, S., Burgos, A., Hardisson, A., Revert, C., 2020. Fluoride levels in supply water from a volcanic area in the Macaronesia region. Environ. Sci. Pollut. Res. 27, 11587–11595. https://doi.org/10.1007/s11356-020-07702-x.

Sarkar, D., Haldar, A., 2005. Physical and Chemical Methods in Soil Analysis: Fundamental Concepts of Analytical Chemistry and Instrumental Techniques. New Age International, New Delhi. ⟨http://site.ebrary.com/id/10318667⟩.

Saxena, N., 2018. A review on fluoride in ground water: Causes, effects and solutions. Int J. Eng. Res Appl. 8, 21–24.

Stenzel, H.B., 1963. Aragonite and calcite as constituents of adult oyster shells. Science 142, 232–233. https://doi.org/10.1126/science.142.3589.232.

Taylor, M., Elliott, H.A., Navitsky, L.O., 2018. Relationship between total dissolved solids and electrical conductivity in Marcellus hydraulic fracturing fluids. Water Sci. Technol. 77, 1998–2004. https://doi.org/10.2166/wst.2018.092.

Thermo Fisher Scientific, BD Plastipak(TM) plastic concentric luer-lock syringe, 2020. https://www.fishersci.co.uk/shop/products/plastipak-plastic-concentric-luer-lock-syringe/10636531 (accessed May 6, 2020).

Turner, B.D., Binning, P., Stipp, S.L.S., 2005. Fluoride removal by calcite: Evidence for fluorite precipitation and surface adsorption. Environ. Sci. Technol. 39, 9561–9568. https://doi.org/10.1021/es0505090.

United States Environmental Protection Agency, Microwave Assisted Acid Digestion of Sediments, Sludges, and Oils, (2007). U.S. EPA Method 3051A (SW-846).

Vahter, M., Skröder, H., Rahman, S.M., Levi, M., Derakhshani Hamadani, J., Kippler, M., 2020. Prenatal and childhood arsenic exposure through drinking water and food and cognitive abilities at 10 years of age: A prospective cohort study. Environ. Int. 139, 105723 https://doi.org/10.1016/j.envint.2020.105723.

Vijayeeswarri, J., Geethapriyai, M., Ramamurthy, V., 2019. Community level defluoridation of groundwater with limestone derived adsorbent. Process Saf. Environ. Prot. 127, 9–15. https://doi.org/10.1016/j.psep.2019.04.029.

Vinati, A., Mahanty, B., Behera, S.K., 2015. Clay and clay minerals for fluoride removal from water: A state-of-the-art review. Appl. Clay Sci. 114, 340–348. https://doi.org/10.1016/j.clay.2015.06.013.

Wang, Y., Reardon, E.J., 2001. Activation and regeneration of a soil sorbent for defluoridation of drinking water. Appl. Geochem. 16, 531–539. https://doi.org/10.1016/S0883-2927(00)00050-0.

Wentworth, C.K., 1922. A scale of grade and class terms for clastic sediments. J. Geol. 30, 377–392. ⟨https://www.jstor.org/stable/30063207⟩.

Wong, E.Y., Stenstrom, M.K., 2018. Onsite defluoridation system for drinking water treatment using calcium carbonate. J. Environ. Manag. 216, 270–274. https://doi.org/10.1016/j.jenvman.2017.06.060.

World Health Organization., 2004. Fluoride in Drinking-Water. World Health Organization, Geneva (https://www.who.int/docs/default-source/wash-documents/wash-chemicals/fluoride-background-document.pdf).

World Health Organization, 2017. Guidelines for Drinking-Water Quality, 4th ed + 1st add. World Health Organization, Geneva https://iris.who.int/handle/10665/254637.

World Health Organization, Chromium in Drinking-Water, Geneva, 2020. https://iris.who.int/bitstream/handle/10665/338062/WHO-HEP-ECH-WSH-2020.3-eng.pdf.

Yadav, K.K., Gupta, N., Kumar, V., Khan, S.A., Kumar, A., 2018. A review of emerging adsorbents and current demand for defluoridation of water: Bright future in water sustainability. Environ. Int. 111, 80–108. https://doi.org/10.1016/j.envint.2017.11.014.

Yang, M., Hashimoto, T., Hoshi, N., Myoga, H., 1999. Fluoride removal in a fixed bed packed with granular calcite. Water Res. 33, 3395–3402. https://doi.org/10.1016/S0043-1354(99)00052-4.