Field experience of Fluoride Nilogon: a method of fluoride removal from groundwater

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Field trial of a patented fluoride removal method, based on precipitation–adsorption, has been carried out in some villages of Assam, North East India, with groundwater sources containing 1.8–20 mg/l initial [F$^-$] at small community (220 l) and household (15 l) levels. Pre-acidified water containing 0.68 mM phosphoric acid was treated in a crushed limestone bed (1–20 mm) for 3 h and filtered through a sand–gravel filter to retain a desired 0.7 mg/l [F$^-$] with pH of 7.44–7.9 and relevant water quality parameters meeting WHO guidelines. A slightly higher dose can totally remove fluoride. The fluoride removal has been found to be independent of initial [F$^-$]. The units have been showing consistent results till now for over five and half years and 4625 batches of use without requiring any interventions like reactivation, replacement or replenishment of the limestone bed. With consistent removal of fluoride from any initial concentration to a desired concentration, a recurring cost of only Rs 0.005/l of water and an estimated life of the limestone bed of about 50 years or 39,000 batches, this safe, environment-friendly and simple method without requiring electricity, has been gaining popularity as Fluoride Nilogon.

Keywords: Fluoride removal, groundwater, hydroxyapatite, limestone defluoridation, phosphoric acid.

FLUORIDE, a naturally occurring mineral, is essential in small quantities for proper growth and maintenance of teeth and bones in humans. However, its excess consumption causes irreversible damage to teeth and bones, a phenomenon known as dental and skeletal fluorosis[1]. Other effects such as osteoporosis, arthritis, braindamage, cancer and neurological disorders in human and certain health problems in animals are seen due to excess fluoride comsumption[1–3]. Fluoride contamination in groundwater occurs due to geological factors such as dissolution of rocks like fluorite, biotite, topaz, etc. and anthropogenic activities like industrial effluents[4]. Over 200 million people from India, China, Sri Lanka and the Rift Valley nations in Africa are affected by excess fluoride poisoning[2]. In India, groundwater of many states are fluoride-affected[5]. In Assam, North East India, large areas of East Karbi Anglong and Hojai district and some parts in neighbouring areas of Guwahati city are affected by excess fluoride in groundwater[6,7]. The World Health Organization (WHO) prescribes a guideline value of 1.5 mg/l for fluoride in drinking water[2]. However, the Bureau of Indian Standards (BIS) has set a lower permissible limit of 1.0 mg/l for fluoride[8].

Research is ongoing to develop a suitable method for removal of difficult-to-remove fluoride with high efficiency and low cost, while at the same time the method has to be safe, environment-friendly and easy to operate by a layman[9–11]. Researchers have developed several defluoridation techniques to mitigate fluoride contamination, viz. coagulation–precipitation[12], reverse osmosis[13], electro-coagulation[14], nanofiltration[15], ion exchange[16], adsorption[17,18], etc. The Nalgonda technique, based on the coagulation–precipitation technique, was once widely used in India. Now it is losing popularity due to difficulty in pH adjustment, high residual sulphate and aluminium in treated water[14].

Adsorption is one of the most common methods of fluoride removal due to its effectiveness, relatively low cost and easy operation. Several adsorbent materials have been reported for fluoride removal from water, e.g. limestone (calcite)[19–21], hydroxyapatite[19], quartz[19], bauxite[22], gypsum[22], brushite[23], laterite[24], pumice stone[25], rare earth oxides[26], graphene[27], chitosan[28], activated alumina[29], alum[30], and calcined phosphoric acid (PA)-treated lime[31]. Reardon and Wang[32], reported a combined precipitation and adsorption method where CO_2 is passed through fluoride-contaminated water in a limestone bed column for generating Ca^{2+} ions for precipitation of CaF_2. However, handling of CO canisters is not easy for rural applications. Several interesting studies were conducted subsequently by adding other acids to the influent water, before treatment with crushed limestone, where fluoride was removed by both precipitation of fluorite and adsorption of fluoride on limestone surface[21,33–37]. However, fluoride removal by these methods is associated with one or more shortcomings, such as high operational and maintenance costs, low capacity of adsorbent, frequent replacement of parts and involving energy-intensive steps[34].

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Recently, a highly efficient, low-cost, safe and environment-friendly method of fluoride removal, viz. phosphoric acid-crushed limestone treatment (PACLT), had been patented and reported by our research group[38,39]. In this method, water is pre-mixed with 0.01 M PA and then treated in a crushed limestone fixed-bed reactor working in a plug-flow (batch) mode for 3 h. Precipitation of CaF_2, fluorapatite (FAP), and physisorption of fluoride by hydroxyapatite (HAP) formed *in situ* from the reaction between calcium and phosphate ions in the reactor were found to be the dominant mechanisms for fluoride removal in this method[38]. Since a bench-scale pilot test of the method using synthetic fluoride-containing water had shown it to have high potential for practical applications[38], we had decided to conduct a field trial.

Here we present results of the field trial of the PACLT method at a small community scale and household level in some fluoride-affected villages of East Karbi Anglong district. The dose of PA was optimized using fluoride containing natural feed water collected from one of the field sources to remove excess fluoride and retaining about 0.6 mg/l fluoride in the treated water. The performance of the field units was pre-assessed with a small replica of the field unit set-up in the laboratory using feed water collected from the field source. The results of the field trial, its safety and suitability have been discussed.

The field trial has already completed over five and half years, but the units are still working well. The method has already started gaining popularity as Fluoride Nilogon (nilogon meaning removal in Assamese). Despite using for total of 4625 batches (once or twice a day) and even for water with initial fluoride ($[F^-]_0$) as high as 20 mg/l, none of the limestone beds has been exhausted yet, making it impossible for us to carry out a study of regeneration of the limestone bed. The excellent experience of the field trial prompted us to publish the results without waiting for exhaustion of the limestone to facilitate use of this rural technology for the benefit of the needy at the earliest.

Materials and methods

Materials

Limestone used in the field trial was obtained as a gift from Bokajan Cement Factory, Cement Corporation of India, Bokajan, Karbi Anglong. The limestone sample with density 2.59 g/cm^3 was high-purity calcite as evident from chemical composition and XRD analysis[36]. The crude limestone was crushed and segregated to selected chip sizes before use. For dose-optimization experiments, the fluoride stock solution was prepared by dissolving NaF (AR-grade, Merck, Mumbai) in doubly distilled water. Synthetic fluoride containing groundwater was prepared by spiking tap water with fluoride from the stock solution. The composition of the synthetic groundwater was: pH (7.47), Na^+ (60.60 mg/l), K^+ (1.07 mg/l), Ca^{2+} (2.50 mg/l), Mg^{2+} (2.40 mg/l), Hg^{2+} (<0.001 mg/l), F^- (0.20 mg/l), Cl^- (5.4 mg/l), SO_4^{2-} (6.3 mg/l), PO_4^{3-} (0.70 mg/l), hardness as CaCO (80 mg/l) and alkalinity as CaCO (86 mg/l). Analytical-grade PA (Merck, Mumbai) was used in laboratory experiments. Food-grade 85% PA (Lakshita Chemicals, Mumbai) was used in field trials.

Field units

One small community unit of 220 l capacity and five household units of 15 l capacity each were used for the field trial in four different villages of East Karbi Anglong district (Supplementary Figures 1 and 2). The fluoride concentration in water of the selected field sources was found to be in the range 20.0–2.8 mg/l. For the small community system, a 500 l plastic tank was used as the reactor chamber, whereas a 1000 l plastic tank was used as the four-layered sand-crushed limestone–sand–gravel filter-cum-pH corrector. The reactor chamber filled with crushed limestone of size 1–20 mm gave a void volume of 220 l. An additional 500 l plastic tank was used to collect the fluoride-contaminated water supplied by the local public health water supply scheme. For household systems, a 40 l bucket was used as the reactor chamber, containing limestone chips of the same size, giving a void volume of 15 l (Supplementary Figure 2). A four-layered filter-cum-pH corrector was made with another 40 l bucket (Supplementary Figure 2). A 15 l bucket was used for mixing PA to the fluoride contaminated water and for feeding the reactor. However, it was observed later that a simple sand–gravel filter also gave the same result as that of the four-layered filters, and therefore the four-layered filters were replaced by simple sand–gravel filters for the other units installed in the villages.

Dose optimization and pre-assessment of performance

A small replica of the field units was set up in the laboratory for optimization of dose of PA and pre-assessment of the performance of the field units using feed water collected from the field water source of the small community unit. This groundwater supplied by the Public Health Engineering Department, Government of Assam, had fluoride concentration ranging between 5.0 and 4.6 mg/l during the year. Three low-density polyethylene containers were used as mixer, reactor and four-layered filter-cum-pH corrector to make the replica unit (Supplementary Figure 3).

Procedure

Fluoride-contaminated field water, after mixing with appropriate amount of PA, was fed to the reactor and kept for a residence time of 3 h. After 3 h, the water was transferred to the filter. The first time-treated water occupied the void volume of the filter-cum-pH corrector and therefore, fluoride-free water could only be collected from the second treatment onwards, thus allowing enough residence time for the treated water to finally settle with a pH of 7.44–7.90.

Instrumental analysis

The concentrations of fluoride in water were determined using an Orion Multiparameter Kit (Orion 5 Star, pH-ISE-Cond-DO Benchtop) using a fluoride ion selective electrode. Total ionic strength adjustment buffer (TISAB-III) was used to control ionic strength and de-complex fluoride. The pH was determined using another Orion Multiparameter Kit with a pH electrode. The metal ions were determined using an atomic absorption spectrophotometer (AAS, Thermo iCE 3000 series, USA) fitted with a hydride vapour generator.

Results and discussion

Laboratory study

Optimization of PA dose: Defluoridation from groundwater with initial 4.8 ± 0.2 mg/l fluoride, collected from field source, was examined with 0.001 M $[PA]_0$ in the feed water to compare the results with those of the bench-scale pilot test reported earlier with synthetic fluoride containing water[38]. Figure 1 shows the results of fluoride removal versus the number of batches of treatment (*n*). The fluoride removal was found to be somewhat poor initially, which started to improve after ten batches and showed further improvement after 16 batches. The observed initial poor defluoridation may be attributed to possible presence of CaO impurity in the limestone. The CaO impurity may neutralize a part of PA, decreasing the effective concentration of PA for fluoride removal. The alkalinity (as $CaCO_3$) in the field water was found to be 150 mg/l compared to 86 mg/l in the synthetic water used earlier. However, there was no noticeable change in defluoridation due to the higher alkalinity of field water compared to synthetic water. Similarly, there was no effect of presence of slightly higher concentrations of sulphate (60 mg/l) and chloride (20 mg/l) ions in field water compared those in the synthetic water (6.3 mg/l and 5.4 mg/l respectively). During the bench-scale pilot tests, we observed good fluoride removal right from the first batch with a higher $[PA]_0$ dosage of 0.01 M to the feed[38]. Therefore, it was decided to pretreat the crushed limestone bed with 0.01 M $[PA]_0$ before lowering the dose of feed PA to get a desirable effluent fluoride concentration of around 0.7 mg/l for healthy teeth and bones[2].

In order to determine the optimum $[PA]_0$ dose for field trial, fluoride was removed from the field water using the replica unit at different dose of $[PA]_0$. For this experiment, a limestone bed of 10–15 mm chip size was first pretreated with 0.01 M PA to neutralize any lime (CaO) present with limestone, followed by defluoridation with varying doses of $[PA]_0$ in the range 0.01–0.5 mM in the feed field water; Figure 2 presents the results. It was observed that in the presence of 0.01 M $[PA]_0$, fluoride was removed from 4.8 to 0.01 mg/l, which is much below the prescription of WHO for drinking water. On lowering $[PA]_0$ from 0.01 M to 0.7 mM, the effluent $[F^-]$ increased from 0.01 to 0.41 mg/l, still well below the prescription of WHO. On further reducing $[PA]_0$ to 0.6 mM, the effluent

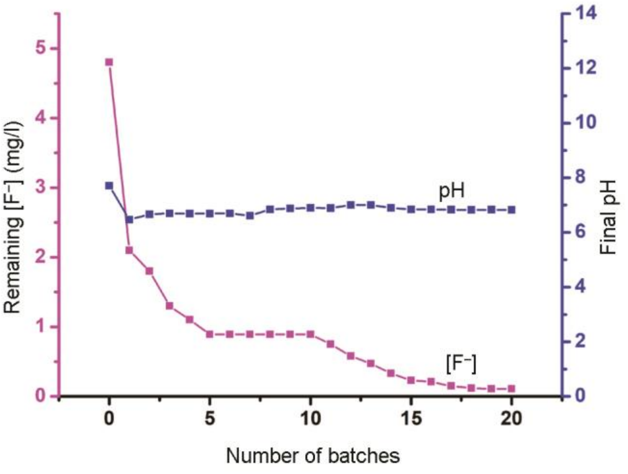

Figure 1. Plots of remaining $[F^-]$ with pH versus the number of batches used in PACLT for fluoride removal in the replica unit from field water with 0.001M $[PA]_0$. $[F^-]_0$ = 4.8 ± 0.2 mg/l.

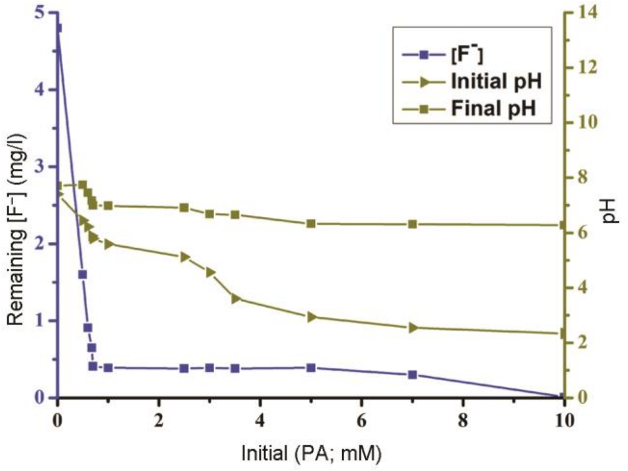

Figure 2. Plots of remaining $[F^-]$ and pH of water before (pH_0) and after (pH_f) treatment in the presence of varying $[PA]_0$ in the replica unit with field water having 4.8 ± 0.2 mg/l of $[F^-]_0$.

[F⁻] increased to 0.91 mg/l. Therefore, $[PA]_0$ of 0.68 mM, which gave an effluent [F⁻] of 0.65 mg/l, was chosen to be the optimum $[PA]_0$ for field trials.

The pH of field water, before and after treatment with $[PA]_0$ ranging from 0.01 M to 0.5 mM was measured (Figure 2). On decreasing $[PA]_0$ from 0.01 M to 0.68 mM, the initial pH of the feed water increased gradually from 2.34 to 5.89. The pH of the treated water increased after treatment in the crushed–limestone reactor, which increased further after passing through the four-layered sand–limestone–sand–gravel filter (Supplementary Figure 3). The effluent pH was below 6.5 with $[PA]_0$ between 0.01 M to 5.0 mM, which is lower than the minimum acceptable limit for drinking water, whereas it was above 6.5 with $[PA]_0$ below 3.5 mM. On the other hand, effluent [F⁻] of 0.91 mg/l and higher was detected with $[PA]_0$ of 0.6 mM and below (with an initial pH of 6.22 and above). However, both desirable effluent [F⁻] of 0.65 mg/l and acceptable pH of 7.37 for drinking purpose were achieved with $[PA]_0$ of 0.68 mM. Therefore, this optimum initial PA concentration was chosen for fixing the dose of $[PA]_0$ for the field trial as 0.463 ml of 8.5% PA per litre of water. However, for convenience of handling, rounded doses of 7 ml and 102 ml of 8.5% PA were used for 15 l household and 220 l small community units respectively.

Pre-assessment of performance: For a quicker assessment of the performance of field units, we examined the performance of the replica unit in the laboratory using fluoride-contaminated groundwater collected from the field source (Supplementary Figure 3). The pre-acidified influent water was poured into the crushed limestone reactor having 1.5 l void volume, allowed a residence time of 3 h and then filtered through a four-layered filter. Figure 3 shows the results. The effluent [F⁻] was within the acceptable range until breakthrough was observed after 250 batches. This means 83 l of defluoridated water was achieved per kilogram of limestone. The final pH of treated water was found to be in the range between 7.10 and 7.70 after passing through the four-layered filter.

Field trial

Performance of the small community field unit: For easy acceptability by the local users, the present fluoride removal method was named as Fluoride Nilogon. Figure 4 shows the results of fluoride removal and final pH of the water after removal of fluoride using the optimized dose of 0.68 mM $[PA]_0$ (102 ml of 8.5% PA in 220 l water) in the small community Fluoride Nilogon unit installed at Dengaon, Karbi Anglong district, on 15 March 2013. The effluent [F⁻] is consistent within 0.6–0.7 mg/l up to 579 batches in over 5½ years, showing no signs of depletion of the limestone till date. The small community field unit has been showing remarkably better performance than the replica unit in the laboratory. It may be noted here that we used crushed limestone chips of size 10–15 mm in the replica unit test in the laboratory. Since it was impractical to choose such a narrow size range of chips for large quantities of limestone, chip sizes of 1–20 mm were used in the small community field unit. The better performance of the field units compared to the replica unit can be attributed to the presence of smaller chip size of limestone in the small community unit. Decrease in the particle size increases the surface area of limestone, thus increasing the removal of fluoride.

The pH of the influent field water was 5.89 with 0.68 mM $[PA]_0$. As the water enters the crushed limestone bed reactor, PA is neutralized by limestone[38]. The pH of the effluent water from the four-layered filter of

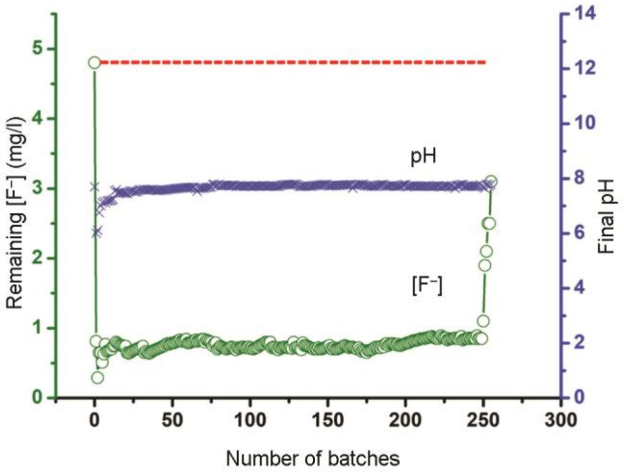

Figure 3. Plots of [F⁻] and pH of treated water versus number of batches for the replica unit $[F^-]_0 = 4.8 \pm 0.2$ mg/l (broken line), $[PA]_0 = 0.68$ mM and residence time = 3 h.

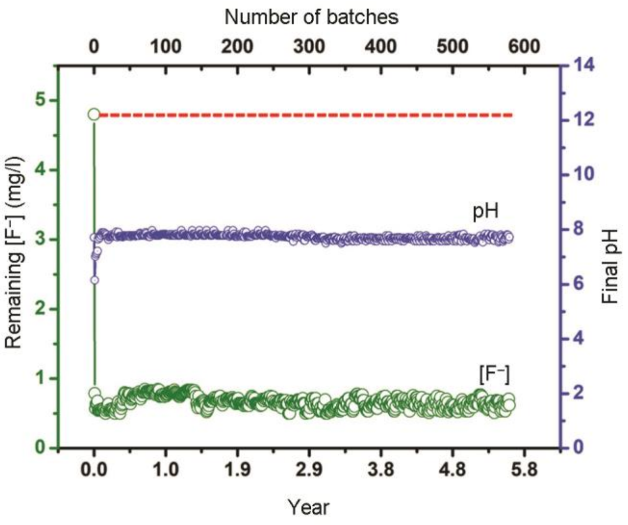

Figure 4. Plots of remaining [F⁻] and pH in treated water versus the number of batches and years of use for the small community field unit. $[F]_0 = 4.8 \pm 0.2$ mg/l (broken line), $[PA]_0 = 0.68$ mM and residence time = 3 h.

the small community field unit has been consistently found to be in the range 7.54–7.90, which is acceptable for drinking.

Performance of the household units: Figure 5 and Supplementary Table 1 show the results of the remaining [F$^-$] and final pH of the treated and filtered water for the household Fluoride Nilogon units with 15 l pore volume installed at the villages of Napakling (H1), Kehang Inglang (H2), Sarik Teron (H3) and Kat Tisso (H4). The results of another household unit installed in Napakling (H5) by a villager, trained by the present authors at Tezpur University, is also included in the figure. H1 was installed on 12 October 2014, while H2, H3 and H4 were installed on 6 December 2014 and H5 was installed on 15 October 2015. The [F$^-$]$_0$ in groundwater of the hand tubewell sources of H1, H2, H3, H4 and H5 was 5.0, 20, 2.8, 5.2 and 4.2 mg/l respectively. The procedure followed for operating the household units was the same as that for the small community unit. The dose of PA was 7 ml 8.5% PA in 15 l water and residence time of water in the reactor was 3 h.

It is interesting to note that the household Fluoride Nilogon units have been showing remaining [F$^-$] in the range 0.50–0.80 mg/l consistently till date, for about four years and up to 4625 batches from the time of installation, thus meeting the WHO guideline value, without any sign of exhaustion of the limestone bed (Figure 5). The effluent pH was in the range 7.4–7.7, which is within the acceptable range pH for drinking water, i.e. 6.5–8.5. Supplementary Table 1 also shows the average values of effluent [F$^-$] and pH obtained from the community and five household systems. The average values were calculated considering all data collected till date. It was observed that in C1, H1, H2, H3, H4 and H5 units, where [F$^-$]$_0$ was 4.8, 5.0, 20, 2.8, 5.2 and 4.2 mg/l respectively, the average effluent [F$^-$] was 0.70, 0.62, 0.59, 0.55, 0.67 and 0.62 mg/l respectively, after treatment. More interestingly, the performance of the present method was found to be independent of initial [F$^-$]$_0$, at least up to 20 mg/l.

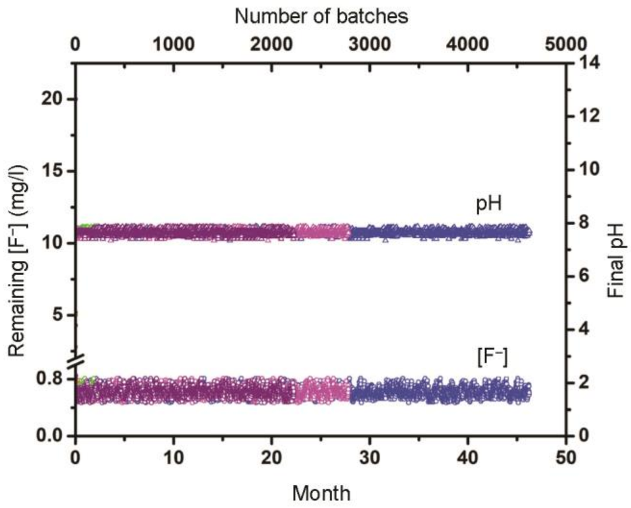

Figure 5. Results of [F$^-$] before and after treatment along with final pH versus the number of batches for the household units: H1 (green), H2 (blue), H3 (magenta), H4 (red) and H5 (purple). [PA]$_0$ = 0.68 mM and residence time = 3 h.

Mechanism of fluoride removal: The observed consistently good fluoride removal without needing any replenishment, regeneration or replacement of the crushed limestone bed for over 4625 batches of use and the method being independent of initial [F$^-$]$_0$ up to 20 mg/l may be attributed to the combined precipitation–adsorption mechanism of fluoride removal using PACLT method[38].

The following reactions have been proposed in the process of fluoride removal by limestone in the presence of PA[38].

$$CaCO_3(s) + 2H_3PO_4 \rightarrow Ca^{2+} + 2H_2PO_4^- + CO_2 + H_2O, \quad (1)$$

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

$$Ca^{2+} + 2F^- \rightarrow CaF_2(s)\downarrow, \quad (3)$$

$$Ca^{2+} + H_3PO_4 + 2H_2O \rightarrow CaHPO_4{\cdot}2H_2O(s)\downarrow + 2H^+, \quad (4)$$

$$5Ca^{2+} + 3HPO_4^{2-} + 3OH^- + F^- \rightarrow Ca_5F(PO_4)_3\,(s)\downarrow + 3H_2O, \quad (5)$$

$$5Ca^{2+} + 3HPO_4^{2-} + 4OH^- \rightarrow Ca_5(OH)(PO_4)_3(s)\downarrow + 3H_2O, \quad (6)$$

$$Ca_5(OH)(PO_4)_3(s) + F^- \rightarrow Ca_5F(PO_4)_3(s) + OH^-. \quad (7)$$

Here, $H_2PO_4^-$ ($pK_{a2} = 7.21$) overshadows HPO_4^{2-} ($pK_{a3} = 12.35$) in the pH range of treated water. The reactions of dissolution of $CaCO_3$ by the triprotic PA ($pK_{a1} = 2.12$), eq. (1), the precipitation of CaF_2, viz. eq. (3) and the precipitation of FAP and HAP, viz. eq. (4–6) are completed rapidly. Due to this, the fluoride concentration in water comes down to about 2 mg/l within 3–4 min[38]. Though FAP has a lower solubility product than that of HAP, high abundance of hydroxide ions in the system makes precipitation of HAP more favourable[40]. The sorption or exchange of the remaining fluoride by HAP (eq. (7)) continues for a longer time as indicated by the continued increase in fluoride removal which lasts for about 3 h along with some adsorption of fluoride by the renewed limestone surface. Thus, it can be stated that defluoridation takes place predominantly through sorption of fluoride by *in situ*-formed HAP, in addition to precipitation of CaF_2 and FAP.

The continued consistent performance of the crushed limestone beds in the field units up to 4625 batches of use (Figure 5) is much better compared to the replica unit which showed breakthrough after 250 batches (Figure 3). This can be attributed to the difference in time interval between two consecutive batches in the field compared to that in the replica unit. While the replica unit was used for four batches a day with about 15 min interval between two batches, the field units were used at the most for two batches in a day and that too with at least 9 h interval between two batches. It is possible that the limestone surface gets enough time to dry and undergo some solid-state reactions increasing porosity or exposure at the surface, which favours dissolution of limestone and subsequent reactions in the next batch. This, however, remains to be verified experimentally. If it is true, along with the fact that the quantity of limestone dissolved by PA (7 ml 8.5% H_3PO_4) per batch of 15 l of water, in a household Fluoride Nilogon unit, is 1.53 g (Supporting Information), the life of the crushed limestone bed of a household Fluoride Nilogon unit may ideally extend to 39,210 batches or 53 plus years. With the field experience till now, this does not seem unlikely.

Plots of average effluent [F^-] versus total alkalinity as $CaCO_3$ of the source water indicate a weak positive correlation between the effluent [F^-] and total alkalinity of the source water with R^2 of 0.901 (Figure 6). However, there is significantly lesser correlation ($R^2 = 0.543$) between the effluent pH and total alkalinity as $CaCO_3$, except at slightly higher pH in the case of the small community unit. It may be noted here that the effluent pH is expected to increase with longer residence time. The effluent water of the small community unit had longer residence time in the filter, which slightly increased the pH.

Potability of treated water: Table 1 presents the relevant water quality parameters before and after treatment measured by standard methods[41]. All the parameters after treatment were within the respective WHO guideline values for drinking water[2]. The concentration of most of the metal ions decreased after treatment, which may be attributed to low solubility of metal phosphates in water. The concentration of Ca^{2+} and PO_4^{3-} also remained within the WHO guideline values.

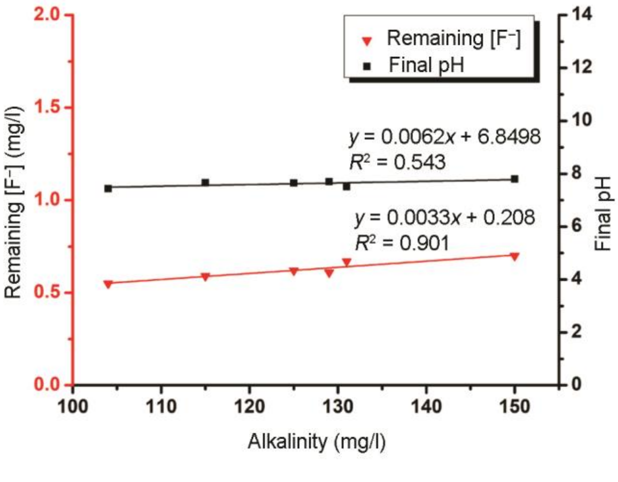

Figure 6. Plots of average value of remaining [F^-] and final pH of treated water of six field units versus the total alkalinity as $CaCO_3$ of the influent water.

Suitability of the method

Capacity of limestone: Analysis of the composition of the precipitate collected from the bottom of the reactor chamber of the replica unit using a spatula, has shown the presence of HAP, FAP and CaF_2, which is consistent with the results reported earlier[38]. The performance of the field units indicates high capacity of limestone in Fluoride Nilogon. However, calculation of the actual capacity is not yet possible as the limestone bed of the community unit has been working consistently for over 579 batches (and 5½ years). Given the field experience, we can assume limestone to work consistently till the entire quantity is dissolved by PA. Considering the use of 7 ml of 8.5% PA twice a day for a household unit, the total number of batches that will be required to dissolve 60 kg (the quantity of limestone required to fill a 40 l drum) of limestone turns out to be 39,210. This means that the limestone bed may work up to a maximum of 53.7 years without needing replacement. This estimate is justified as the limestone beds of the household field units have been working consistently over 4625 batches or about four years. Taking the fluoride removed per batch of a household unit as 19.3 mg/l from the initial 20 mg/l, the estimated capacity of fluoride removal till total exhaustion of the limestone turns out to be 252.2 mg/g. This is incomparable to the capacity of limestone alone (0.39 mg/g)[42], activated alumina (1.08 mg/g)[43], activated carbon (1.10 mg/g)[44], bone char (1.4 mg/g)[45] and HAP nanoparticles (5.5 mg/g)[46].

Cost estimation: For estimation of the recurring cost incurred in Fluoride Nilogon, one needs to take only the cost of PA into account. The cost of limestone can be included in capital cost as it has almost unlimited lifetime, as mentioned in the previous section. There is no maintenance cost of the units. Thus, considering the market retail price of 85% PA as Rs 100, the recurring cost of the treatment turns out to be Rs 0.00467/l (USD 0.000063) of treated water, which is much lower than that of RO (≈ Rs 0.54 considering Rs 6000 for annual maintenance and 30 l water consumption per day) and any adsorption-based fluoride filters. The capital cost includes only the cost of two plastic containers of desired size, two taps, crushed limestone, sand and gravel. The capital cost turns out to be Rs 600 (USD 8.51) and Rs 4500 (USD 61.12) for the household and small community Fluoride Nilogon units respectively (Supporting Information).

Table 1. Relevant water quality parameters before and after treatment by PACLT

Parameter (mg/l except for pH)	WHO guidelines value	Before treatment	After treatment
pH	6.50–8.50[a]	7.40	7.3–7.5
Dissolved solids	600	175	240
Suspended solids	NS[b]	12	8
Total alkalinity as $CaCO_3$	200	150	154
Total hardness as $CaCO_3$	200	154	160
Phosphate	NS	0.135	0.109
Sulphate	500	60	62
Chloride	250	20	7
Nitrate	50	0.45	0.27
Cadmium	0.003	<0.001	<0.001
Calcium	50	10.78	12.13
Chromium	0.05	ND[c]	ND
Cobalt	NS	ND	ND
Copper	2.0	<1.00	<1.00
Lead	0.01	<0.001	<0.001
Magnesium	NS	2.81	3.40
Manganese	0.40	<0.001	<0.001
Zinc	3.0	2.5	0.07
Sodium	200	94.69	85.96
Potassium	NS	4.22	3.12
Iron	0.30	0.013	<0.001

$[PA]_0 = 0.68$ mM; $[F^-]_0 = 4.8 \pm 0.2$ mg/l; Source of water sample: piped water supply by PHED.
[a]Acceptable range for drinking; [b]NS, Not specified and [c]ND, Not detectable.

Sludge disposal: A toxicity characteristic leaching procedure test prescribed by the United States Environmental Protection Agency (US EPA) was performed on the precipitate produced in the reactor, which showed only 0.35 mg/l fluoride in the leachate. Thus, leaching from the sludge of Fluoride Nilogon is 429 times lower than the maximum permissible limit of 150 mg/l allowed for land-fill dumping by US EPA[47,48]. The very low leaching from the sludge may be attributed to the strong binding of F^- in FAP. The solid sludge can be easily disposed of in landfills or buried in other safe places like construction sites. However, the question of sludge disposal may not arise now, as the limestone bed is still in a good condition even after 4625 batches of use, and ideally the life of the limestone bed may extend over 53 years.

User satisfaction and present status: Limestone, a low-cost sedimentary rock, is readily available in most of the fluoride-affected areas of the world, including India[49]. In Assam, limestone mines are present in the vicinity of its severely fluoride-affected areas of West Karbi Anglong and Hojai districts. PA is approved by the US EPA for application in water purification[47]. PA is also easily acceptable to people as it is an edible acid used in popular beverages and for preserving packaged food. The treated water does not leave any objectionable odour or colour. Moreover, PA being a weak acid is easy to handle. However, in the present field study, PA has been dispensed to the rural users after ten times dilution from the original strength of 85% (W/V) for further safety.

That the users are satisfied with the Fluoride Nilogon is indicated by continuation of the field trial units by them for over five and half years continuously. There is an increasing desire of the affected people to acquire a household unit of their own. Government restrictions on procurement of limestone are however a great deterrent faced by the villagers. Despite that, there are six small community and 35 household Fluoride Nilogon units at present in West Karbi Anglong district, most of which have been installed by trained local people. With involvement of various individuals and government and non-governmental organizations, e.g. Karbi Anglong Autonomous Council, National Programme for Prevention and Control of Fluorosis, and Art of Living, Fluoride Nilogon is set for implementation in a big way soon in Karbi Anglong.

Conclusion

The present field study proves that Fluoride Nilogon, is a good rural technology for fluoride removal. The method involves pre-mixing of fluoride-contaminated water with a dose of 0.463 ml of 8.5% PA/l of water to give a concentration of 0.68 mM of PA in water, subsequent treatment of the water in a fixed-bed crushed limestone reactor of chip size 1–20 mm for 3 h, and then sand–gravel filtration. The crushed limestone bed needs to be pretreated with 0.01 M PA. The method removes excess fluoride efficiently from as high as 20 mg/l to a desired level of 0.7 mg/l. The removal is independent of the initial $[F^-]$ and a higher dose of PA can totally remove fluoride. The pH of the treated water remains within 7.4–7.9, which is in the middle of the acceptable range of

6.5–8.5 for drinking. All other relevant water quality parameters for the treated water remain within the guideline values of WHO.

The field units have been working consistently over 4625 batches or 5½ years without needing any interventions like regeneration, replenishment or replacement of the limestone. The estimated life of the crushed limestone bed of a household Fluoride Nilogon unit used twice a day with 20 mg/l feed water is 39,210 batches or over 50 years. The recurring cost of the treatment which includes only the cost of PA is Rs 0.00467 (USD 0.000063)/l of treated water. This is much lower than any other fluoride removal methods. Requiring only two containers, two taps, limestone, sand and gravel, the capital cost of 15 l household and 220 l small community Fluoride Nilogon units is only Rs 600 (USD 8.51) and Rs 4500 (USD 61.12) respectively. Finally, it can be concluded from the present field experience that, high efficiency, high capacity of limestone, extremely low cost, safe, environment-friendliness, non-requirement of electricity, non-requirement of regeneration, replenishment or replacement of any part for years (possibly decades), simple enough to be operated by a layman and user satisfaction prove Fluoride Nilogon as a good rural technology to address the worldwide problem of excess fluoride in drinking water.

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