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# Column evaluation of a water defluoridation technique based on phosphoric acid-enhanced limestone adsorption

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Fluoride removal from water by phosphoric acid-enhanced limestone defluoridation has been studied in a continuous-flow mode using crushed limestone column by adding dilute phosphoric acid (PA) to the influent water. The flow rate of the gravitationally fed water in an up-flow mode is controlled with a flow controller. Fluoride has been removed from initial 5 mg/L to 0.1 mg/L using 0.01-0.05 M initial PA. The *p*H of the treated water was between 7.4 and 7.7. The present continuous-flow mode show almost four times higher fluoride removal capacity of the limestone than that of the batch mode reported earlier. The continuous-flow mode also shows better regeneration of the exhausted limestone and lower recurring cost compared to that of the batch mode. The kinetic and mechanistic behaviour of fluoride removal in the continuous-flow mode has been found to be somewhat different from that of the batch mode. Three stages of fluoride removal observed as a function of throughput volume have been attributed to gradually diminishing precipitation and sorption of fluoride as the limestone surface is gradually covered by adsorbed fluoride, and precipitate of calcium carbonate and fluoroapatite.

**Keywords:** Limestone defluoridation, Phosphoric acid, Hydroxyapatite, Breakthrough analysis, Regeneration studies

Fluoride contamination in drinking water had been recognised as one of the most serious health problems of worldwide concern. Although small concentration of fluoride may be beneficial for health, excessive intake of fluoride causes dental and skeletal fluorosis[1,2]. World Health Organisation (WHO) and Bureau of Indian Standard (BIS) had set the permissible limits for fluoride in drinking water as 1.5 mg/L and 1.0 mg/L, respectively[3,4]. When the fluoride concentration in drinking water exceeds 1.0-1.5 mg/L, dental fluorosis occur which is characterized by opaque white patches, staining and pitting of teeth[1]. Skeletal fluorosis occurs when contamination level of fluoride in drinking water exceeds 4 mg/L[5]. Use of alternate fluoride-free water sources, *viz.*, surface water and rain water were the best solution to get rid of fluoride contamination. However, in the absence of alternate safe water and due to difficulty in piping safe water to remote and sparse habitations, there is an urgent need of effective and low-cost fluoride removal techniques in developing countries.

The available techniques for removal of excess fluoride from contaminated water were based on adsorption[6,7], coagulation followed by precipitation[8], ion-exchange[9], nanofiltration[10], reverse osmosis[11], electroldysis[12], electrocoagulation[13], etc. Adsorption is preferred for defluoridation of water because of its simplicity and cost effectiveness. Limestone (calcite)[14-17], gypsum[18], raw bauxite[19], magnesite[19], pumice stone[19], alumina[20], zeolites[21], clays[22], charcoal[23], rare earth oxides[24], bleaching earth[25], hydroxyapatite (HAP)[6,14,26], surfactant-modified pumice[27], tamarind fruit shell carbon[28], graphene[29], etc., are examples of common fluoride adsorbents. However, most of the adsorbents involve high operational and maintenance costs or energy-intensive steps. Limestone, a low-cost and abundant geomaterial, has been used widely for fluoride removal by many researchers[14,30].

Reardon, *et al.*, has reported earlier that limestone ($CaCO_3$) in presence of $CO_2$ can reduce fluoride from initial 10 mg/L to below 2 mg/L due to the precipitation of $CaF_2$ by $Ca^{2+}$ ions generated in situ through the dissolution of limestone[15]. Turner *et al.* reported increased fluoride removal by limestone in presence of mineral acids and showed that both precipitation as well as adsorption of fluoride on limestone surfaces contributes to the fluoride removal[16]. As such, handling strong acids by rural people is unsafe. Moreover, the use of $HNO_3$ leaves high residual of $Ca^{2+}$ and toxic $NO_3^-$ ions in treated water[31]. An adsorbent prepared by calcinations of PA treated limestone powder has been reported recently to be effective in fluoride removal. However, the calcination is an energy-intensive step[32,33]. Thus, an efficient, low-cost, environment-friendly method that uses easily available material, has minimum periodic replacement, can be run without electricity and is simple enough to be operated by a layman in rural condition still remains as a challenge to the researchers.

Nath and Dutta reported an acid-enhanced limestone defluoridation (AELD) where the influent water was pre–acidified with weak edible acids, *viz*., acetic acid (AA), citric acid (CA) or oxalic acid (OA) was treated with fixed-bed crushed limestone column in a batch mode[34-36]. The mechanism of fluoride removal in the AELD was shown to be a combination of precipitation of $CaF_2$ and adsorption of fluoride on limestone surface renewed by dissolution by the acid. Though the efficiency of fluoride removal was satisfactory, the capacity of limestone for fluoride removal was low. Recently, we have reported up to 99% fluoride removal efficiency along with a considerable increase in the defluoridation capacity of limestone by using PA[31,37] in place of the organic acids. The increased fluoride removal in the PA–enhanced limestone defluoridation (PAELD) was attributed to the in situ formation of calcium phosphates, *viz*., HAP which is a strong adsorbent of fluoride[6,14,26], in addition to the other mechanisms of fluoride removal operative in the case of AELD with other acids[34-36]. With competitive efficiency, capacity and cost; environment-friendliness and simplicity of operation; the PAELD in the batch mode was shown to be a potential fluoride removal technique[31].

The present paper describes a study on the PAELD method in a continuous-flow mode, carried out considering the advantage of the continuous-flow mode over batch mode for an online domestic application. The fluoride removal in the continuous flow mode has been evaluated for varying concentrations of PA ($[PA]_0$) and fluoride ($[F^-]_0$) in the influent water at varying flow rates. The regeneration of the exhausted limestone has been studied. The fluoride removal performance along with the kinetic and mechanistic behaviours of the removal in the continuous-flow technique has been compared with that of the batch mode.

## Experimental Section

### Materials

The crude limestone sample, obtained from Bokajan Cement Factory, Bokajan, Assam, India, was a high quality calcite as indicated by chemical and XRD analysis[34]. The crude limestone was crushed and segregated into different particle size, *viz*., 1.0-1.5 cm for column experiment. Working solutions were prepared by diluting the stock solution which was prepared by dissolving 2.2102 g of AR NaF (Merck, Mumbai) in 1000 mL double distilled water. TISAB-III (total ionic strength adjusting buffer solution) was used to control the ionic strength and de-complex fluoride in the test solutions. PA obtained from Merck was used to acidify fluoridated water to different influent concentrations.

### Methods

#### *Continuous flow column experiment*

Plexiglass columns of length 90 cm and radius 6 cm containing crushed limestone chips of 1.0-1.5 cm size was placed vertically as shown in Fig. 1. The void volume in such a fixed bed column was approximately 1500 mL, which was about 43% of the total inner volume of the limestone-filled column. The influent water was prepared by mixing $[F^-]_0$ in the range of 5-10 mg/L and $[PA]_0$ in the range 0.01-0.05 M. A large flat plastic (LDPE) container, kept at about 1.5 m above the column to minimise variation in flow rate, was used as a feed reservoir for influent water containing fluoride and PA. The feed reservoir was placed at a level above the outlet at the top of the column to maintain a nearly constant gravity feeding in an up-flow mode. The influent water was allowed to enter the column from its bottom with different flow rate controlled by a flow controller. A plastic container of radius 8 cm open at the bottom towards the column and having a hole at its bottom side wall was placed at the top of the column for collecting the overflowing effluent water. The effluent water, so collected was then treated in a four layered sand-limestone-sand-gravel filter for *p*H correction as shown in Fig. 1.

#### *Column regeneration*

After breakthrough, the exhausted limestone columns were fed with 0.30 M NaOH (*p*H = 12.00) solution in the up flow mode at different flow rates. The cycle was continued until the concentration of fluoride in the effluent water attained equilibrium. After the alkali treatment, the column was flushed with fluoride free water to remove the remaining alkali. The fluoride removal experiment was then repeated until the breakthrough was observed. All the experiments are done in triplicate.

### *Analytical methods*

[F⁻] was measured on an Orion Multiparameter Kit (Model: 4–Star pH.ISE Benchtop) using an Orion ion selective electrode (ISE) for fluoride. TISAB-III buffer solution was added to sample solutions in the ratio of 1:10. The calibration of the ion meter was done at 0.1, 1.0, 10, mg/L [F⁻]. The *p*H was measured on a multiparameter kit (model 5Star *p*H.ISE.Cond.DO Benchtop, Orion, USA). The Fourier transform infrared spectrum (FTIR) spectra were recorded using Nicolet Impact-410 IR spectrometer in the range of 4000-500 $cm^{-1}$ in KBr medium. The X-ray diffraction (XRD) analysis was carried out in a Rigaku Miniflex Xray diffractometer with Cu–Kα radiation (λ= 0.154 nm) at 30 kV and 15 mA at a scanning range of 2θ =10–70°. SEM–EDX micrographs were taken on a scanning electron microscope, (SEM, model JSM–6390LV, Jeol, Japan). The metal ions in water before and after treatment were determined by using atomic absorption spectrophotometer (AAS, model Analyst 200, Thermo iCE 3000 series, USA). The presence of other ion concentrations were determined by UV–visible spectroscopic measurements was done on a Shimadzu UV–2550.

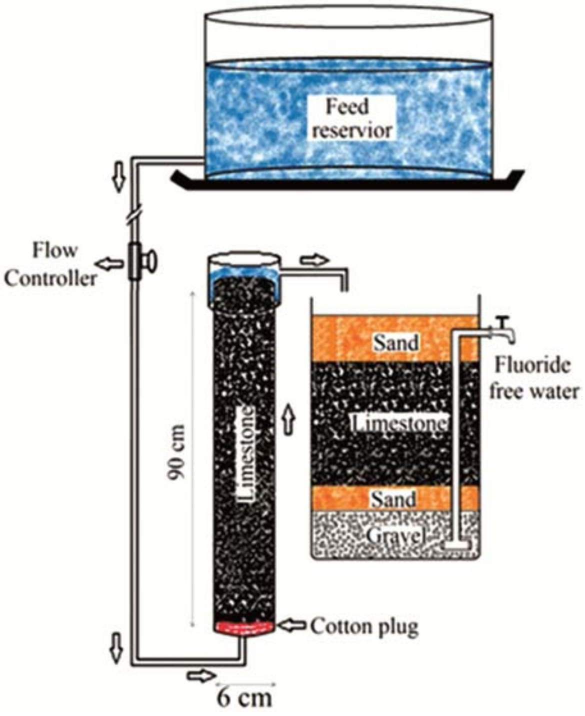

Fig. 1 — The experimental set up for continuous flow test.

### Statistical analysis

The least significant difference (LSD) amongst the data of fluoride removal with $[PA]_0$, $[F^-]_0$, and flow rates were analysed by one way analysis of variance (one–way ANOVA). All the statistical analyses were performed using SPSS 16.

## Results and Discussion

### Fluoride removal performance

The fluoride removal performance was studied at different $[PA]_0$ and $[F^-]_0$ at different flow rates and after regenerations of the exhausted limestone. Formation of a small amount of white powder was observed in the limestone column but, interestingly, no clogging in the column was observed during any of the experiments.

### Effect of influent PA concentration

Figure 2 shows the removal of fluoride from $[F^-]_0$ of 5 mg/L at the flow rate of 100 mL/h in presence of different $[PA]_0$. It has been found that fluoride is removed from 5 mg/L to 0.1-1.0 mg/L and the removal can be continued up to many cycles using the same limestone bed. The performance of limestone for fluoride removal in presence of PA is found to be better than that reported in limestone defluoridation using other acids[34-36]. This indicates a major contribution to the removal by calcium phosphates formed in the column due to reaction between the phosphate ions of PA and calcium ions formed by the dissolution of limestone. The fluoride removal was found to increase significantly with increase in $[PA]_0$

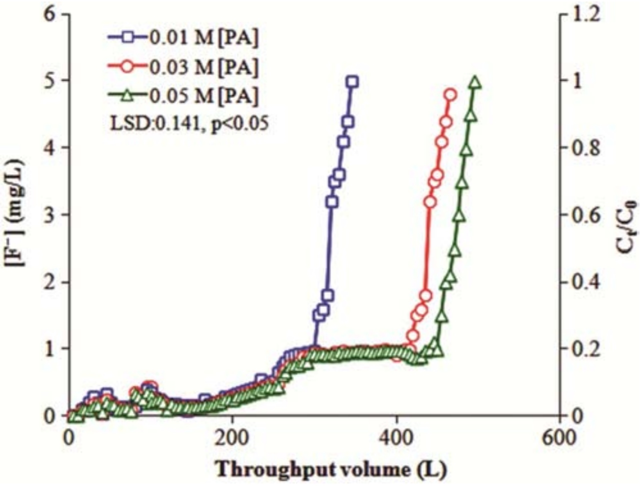

Fig. 2 — The breakthrough curves for fluoride removal at different $[PA]_0$ at $[F^-]_0$ = 5 mg/Land flow rate = 100 mL/h.

with an LSD value 0.141 at $p<0.05$. The breakthrough was reached sooner at lower $[PA]_0$. However, 0.01 M influent PA is sufficient to reduce fluoride concentration from influent 5 mg/L to less than 1 mg/L. A quantity of 300 L of water could be defluoridated before the breakthrough in the presence of 0.01 M $[PA]_0$. Further experiments were performed with 0.01 M PA concentrations as low acid concentration is more suitable in field applications.

### Effect of influent fluoride concentration

The removal of fluoride was studied from $[F^-]_0$ of 5, 7 and 10 mg/L at a fixed $[PA]_0$ of 0.01 M and flow rate of 100 mL/h (Fig. 3). The breakthrough was observed sooner with higher $[F^-]_0$. With $[F^-]_0$ of 5 mg/L, a total volume of 300 L of fluoride free water was obtained without regeneration of the limestone and the throughput volume was significantly decreased with increasing $[F^-]_0$ with LSD value 0.220 at $p<0.05$.

### Effect of flow rates

The fluoride removal performance was examined at different flow rates of the feed, and hence of the output also, at $[F^-]_0$ of 5 mg/L in presence of 0.01 M $[PA]_0$. The results are summarized in Fig. 4a. About 300, 225 and 55 L breakthrough volume ($V_B$) s of water were obtained at flow rates of 100, 200 and 300 mL/h, respectively, before the $[F^-]$ in the effluent reached 1.5 mg/L, the WHO guideline value.

The service time at breakthrough ($t_b$) and empty bed contact time (EBCT) have been evaluated using the Eqs (1) and (2)[38,39]:

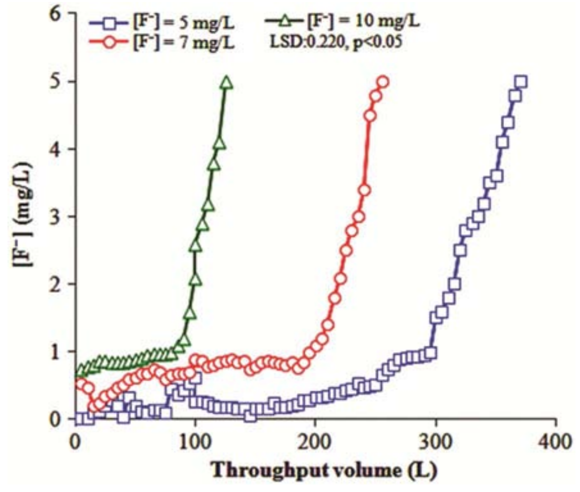

Fig. 3 — The breakthrough curves for defluoridation of water at different influent fluoride concentrations at $[PA]_0$ = 0.01 M and flow rate = 100 mL/h.

$$t_b = V_B/Q \quad \text{... (1)}$$

$$\text{EBCT} = V/Q \quad \text{... (2)}$$

where, V (mL) and Q (mL/h) are bed volume and flow rate. EBCT is defined as the time a fluid spends in the empty column[38]. The results indicate that a decrease in flow rate increased the breakthrough volume or breakthrough time due to an increase in empty bed contact time, which was 3000, 1150 and 183 min for flow rates at 100, 200 and 300 mL/h, respectively (Table 1). Thus, the fluoride removal significantly increases with decreasing flow rate with LSD value 0.026 at $p<0.05$.

### The *p*H of treated water

The final *p*H of the treated water is an important parameter. The *p*H of the treated water of each sample measured till the onset of breakthrough and the results were plotted against the throughput volume (L) for different flow rates (Fig. 4b).

The influent *p*H was 2.34 at $[PA]_0$ of 0.01 M. As the influent water enters into the column containing

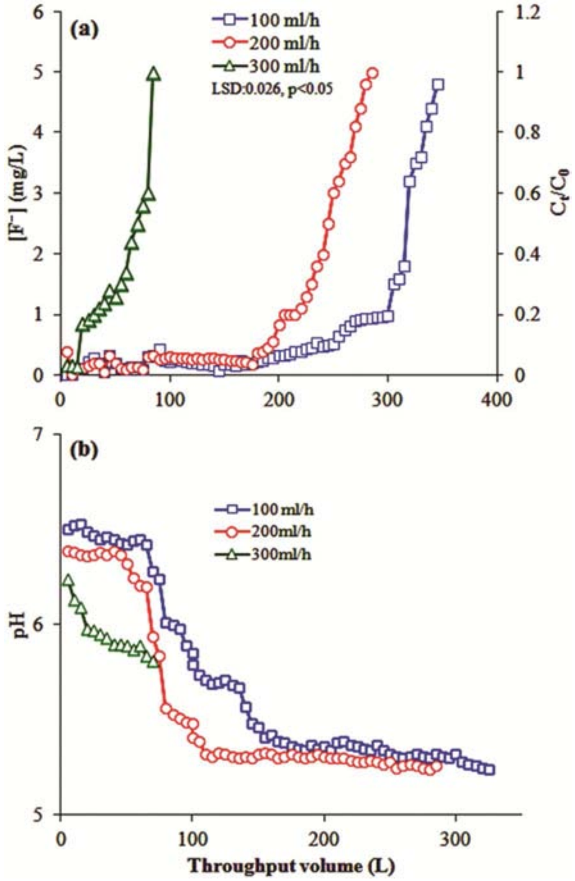

Fig. 4 — The plots of (a) breakthrough curves and (b) remaining pH of effluent water *vs*. throughput volume (L), at different flow rates with $[PA]_0$ = 0.01 M and $[F^-]_0$ = 5 mg/L.

Table 1 — Summary of breakthrough results for fluoride removal in fixed–bed column PAELD at varying flow rates.

| Flow rate (mL/h) | V (L) | $t_b$ (h) | $V_B$ (L) | EBCT (min) |
|---|---|---|---|---|
| 100 | 650 | 3000 | 300 | 390 |
| 200 | 650 | 1150 | 230 | 195 |
| 300 | 650 | 183 | 55 | 132 |

limestone bed, the acidified water gets neutralized by limestone through a reaction in Eq. (3)[31]:

$$CaCO_3 + 2H_3PO_4 \rightarrow Ca^{2+} + 2H_2PO_4^{-} + H_2O + CO_2\uparrow \quad \text{... (3)}$$

The *p*H of the effluent from the reactor was found in the range of 6.5-5.3. The effluent *p*H was found to increase with decrease in flow rate suggesting the neutralization to be a slow process. The *p*H decreased with increase in the throughput volume indicating inhibition of the neutralization reaction at the limestone surface by some process, e.g., sorption of fluoride, which decreases the contact between limestone surface and PA of water. The slightly acidic effluent *p*H is corrected to 7.4-7.7 (acceptable range for drinking) by the treatment in a four layered sand-limestone-sand-gravel filter (Fig.1) for a residence time of 1 h.

### Column regeneration

Since regeneration increases the commercial viability and environmental acceptability of a water purification technology, we have regenerated the exhausted limestone by feeding 0.30 M NaOH solution through the column at different flow rates until $[F^-]_0$ attained equilibrium at 0.27 mg/L. Figure 5a shows the breakthrough curves of PAELD with limestone after the first time regeneration at three different flow rates at $[F^-]_0$ of 5 mg/L and $[PA]_0$ of 0.01 M. The first–time regenerated limestone showed fluoride removal activity of about 75% compared to fresh limestone. In the regeneration of exhausted limestone, at *p*H 12.00 with 0.30 M NaOH, the $OH^-$ ion may replace $F^-$ ion of surface of fluoroapatite (FAP) products and exhausted limestone. The activity of the regenerated limestone was also found to decrease with increasing flow rates as expected. To see the activity of exhausted limestone, we have performed three times regeneration experiment after completion of each regeneration cycle (Fig. 5b). The activity of the regenerated limestone was found to decrease more with repeated regeneration as shown in Fig. 5b.

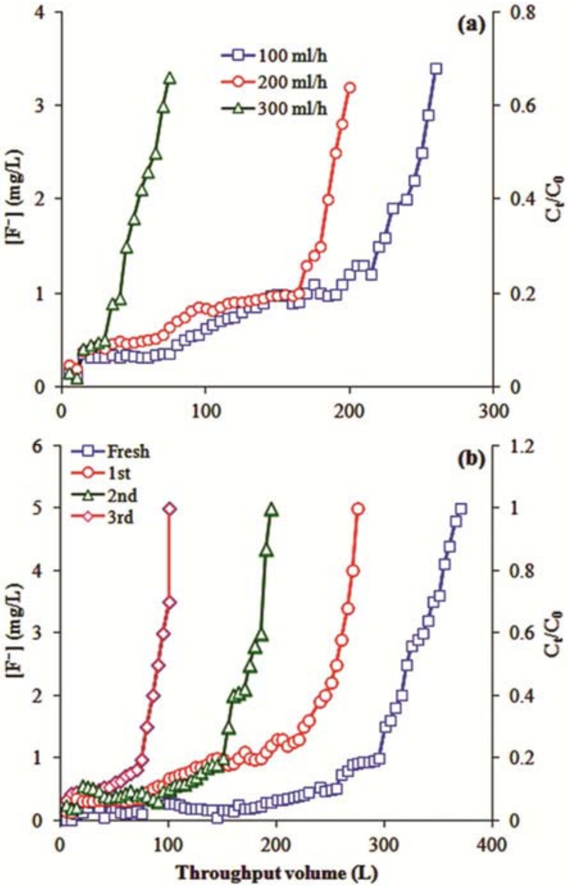

Fig. 5 — The breakthrough curves for (a) fluoride removal with 1st time regenerated limestone and (b) fresh limestone and three successive regenerations of the same limestone at different flow rates with $[F^-]_0$ = 5 mg/L and $[PA]_0$ = 0.01 M.

### Mechanism of fluoride removal

The major characteristics of the FTIR, XRD and SEM–EDX spectrum of the precipitate, collected after breakthrough in continuous flow PAELD method (Fig. S1–3 of Supplementary Information), were found to be similar to that of the batch mode[31]. However, the 1430 $cm^{-1}$ peak was absent in the FTIR of the precipitate indicating the absence of $CaCO_3$ in the sample unlike that of the batch process[31]. Moreover, an additional peak found at 1226 $cm^{-1}$ corresponding to $H–PO_4^{2-}$ stretching was found in the precipitate in the present case[40]. Thus, the precipitate collected after breakthrough in continuous flow PAELD method is predominantly calcium phosphate unlike that of the batch mode where the precipitate consist significant quantity of $CaCO_3$ also. A quantitative determination of $F^-$ content in the precipitate formed in the reactor, using a standard procedure[41], showed about 1.2 mg/L $F^-$ which confirms the sorption of fluoride by HAP.

### Saturation index

The fluorite Saturation Index ($SI_f$) has been calculated using the equation below[16]:

$$SI_f = \log_{10} (Q/K_{sp}) \quad \ldots (4)$$

where, Q = (activity of $Ca^{2+}$)(activity of $F^-$)$^2$ and $K_{sp}$ is the solubility product of fluorite, $3.5\times10^{-11}$. The $[F^-]$ and $[Ca^{2+}]$ in the treated water are very low and hence taken as equal to their respective activities. The $SI_f$ of the experiment with fresh limestone at 0.01, 0.03 and 0.05 M $[PA]_0$ and with regenerated limestone (Fig. 6) provides some interesting information:

i. The $SI_f$ were found to be higher with higher $[PA]_0$ which may be attributed to an increase in $[Ca^{2+}]$ in the effluent water due to an increasing dissolution of limestone at higher $[PA]_0$.

ii. The $SI_f$ values were negative in all cases, except towards the breakthrough with 0.05 M $[PA]_0$, indicating a dominant role of sorption of fluoride in the removal of fluoride[15,31]. There is a highly efficient fluoride removal, to far below 1 mg/L, at low throughput volume (Figs 2–5). This can be attributed to sorption of fluoride in addition to precipitation as precipitation alone can remove fluoride only to below 2 mg/L as limited by the solubility product of $CaF_2$[15]. Probably, the relatively rapid precipitation[36] quickly brings down the fluoride from any initial concentration to about 2 mg/L and after that the relatively slow sorption process comes into play.

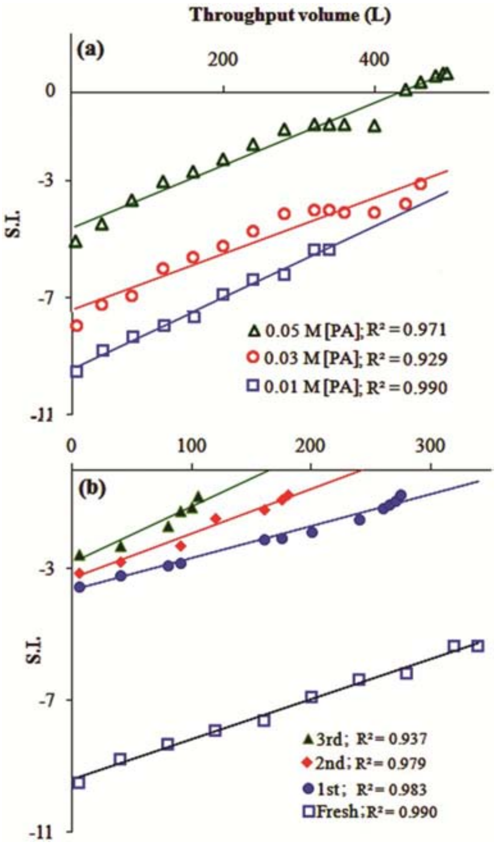

Fig. 6 — The saturation index of fluorite ($SI_f$) for the continuous flow PAELD experiment: (a) with $[PA]_0$ of 0.01, 0.03 and 0.05 M; and (b) with regenerated limestone.

iii. The $SI_f$ values increased almost linearly with the throughput volume. Therefore, the observed increase in the $SI_f$, at a fixed flow rate, is due to a decrease in sorption of fluoride and not due to any increase of the precipitation. From the linear plots of SI *vs*. V, we find

$$SI = mV + C \quad \ldots (5)$$

where, V is the measured throughput volume, and m and C are experimentally determined constants which are characteristic of $[PA]_0$, $[F^-]_0$, flow rate and the limestone quality. Thus, from Eqs. (4) and (5) we get (see Supplementary Information S1),

$$[F^-] = (K_{sp}e^{mVC}/[Ca^{2+}])^{1/2} \quad \ldots (6)$$

Therefore, the $[F^-]$ in the effluent water and hence the breakthrough point can be determined indirectly for a set of fixed conditions of the process by determining the $[Ca^{2+}]$. It may be noted that monitoring effluent $[F^-]$ through determination of $[Ca^{2+}]$ using a flame photometer in rural areas should be easier than the determination of $[F^-]$ using an ISE.

iv. The $SI_f$ value increased considerably after first regeneration of the column and then slightly increased after further successive regenerations. This suggests that the sorption of fluoride considerably decreased after the first regeneration and the decrease continued after subsequent regenerations.

### Removal efficiency and mechanism

It can be seen from the pattern of remaining $[F^-]$ in Figs 2-5 that the $[F^-]$, before breakthrough, increases with each regeneration. In fact, there are three different levels of fluoride removal. The first one is a very good removal to below 0.5 mg/L which is prominent with fresh limestone and towards the beginning of the use of the limestone, the second one is a moderately good removal to between 0.5 and 1 mg/L after use of the limestone for some time and the third one is a fairly good removal to between 1 and 2 mg/L towards the last stage of the activity of the limestone. It is known that precipitation alone cannot remove fluoride to below 2 mg/L whereas adsorption can remove fluoride to any low level[15,37].

Based on the present findings one can attribute the observed stages of fluoride removal as a function of the throughput volume as follows:

i The initial very good fluoride removal to near 0.1 mg/L may be due to an unabated precipitation of fluoride and an unabated sorption of fluoride on abundant original adsorption sites of limestone surface and by HAP.

ii The good fluoride removal to 0.1-0.5 mg/L may be due to an unabated precipitation and a reduced sorption by HAP and limestone surfaces renewed by precipitation.

iii The moderately good fluoride removal to 0.5-1.0 mg/L may be due to a gradually diminishing precipitation and sorption due to covering of limestone surface by adsorbed fluoride and deposition of inactive precipitates like $CaCO_3$.

iv Finally, the onset of the breakthrough may be due to cessations of both the precipitation and the sorption processes.

Table 2 — The water quality parameters of water before and after treatment in the PAELD in the continuous flow mode with $[PA]_0 = 0.01M$, $[F^-]_0 = 5$ mg/Land flow rate of 100 mL/h.

| Parameter in mg/L except for *p*H | WHO guideline value | Before treatment | After treatment |
|---|---|---|---|
| *p*H | 6.50-8.50[a] | 7.47 | 7.4-7.7 |
| Dissolved solid | 600 | 130 | 156 |
| Suspended solid | NS[b] | 10 | 4 |
| Total alkalinity as $CaCO_3$ | 200 | 80 | 84 |
| Total hardness as $CaCO_3$ | 200 | 80 | 95 |
| Sulphate | 500 | 6.3 | 6.2 |
| Phosphate | NS | 0.70 | 0.74 |
| Nitrate | 50 | 0.55 | 0.20 |
| Cadmium | 0.003 | 0.001 | <0.001 |
| Calcium | 50 | 2.50 | 3.76 |
| Chromium | 0.05 | ND[c] | ND |
| Cobalt | NS | ND | ND |
| Copper | 2.0 | 1.00 | 1.20 |
| Lead | 0.01 | ND | ND |
| Magnesium | NS | 2.4 | 2.9 |
| Manganese | 0.40 | 0.10 | 0.09 |
| Zinc | 3.0 | 2.0 | 0.08 |
| Sodium | 200 | 60.6 | 60.0 |
| Potassium | NS | 1.07 | ND |
| Iron | 0.30 | 0.34 | 0.085 |

[a]Acceptable range for drinking, [b]NS: Not specified, [c]ND: Not detectable

### Suitability analysis

#### *Safety*

The relevant water quality parameters of the treated water samples before and after PAELD treatment determined using standard methods[42] are given in Table 2. All the water quality parameters after treatment were within the respective WHO guideline values for drinking water[3]. The concentrations of most of the metal ions showed a decrease after treatment. The concentrations of $Ca^{2+}$ and $PO_4^{3-}$ which are components in the materials used in the present method also remained within the WHO guideline values and that of concentration of $NO_3^-$ was slightly decreased after treatment.

It can be mentioned here that a toxicity characteristic leaching procedure (TCLP) test[43] on the precipitate has shown a leaching of 0.21 mg/L which was about half of that observed in the batch mode case[31] and much less than the permissible value of 150 mg/L for disposal in landfill[44].

### Capacity of limestone and cost–benefits analysis

The removal of fluoride was found to be better at the flow rate of 100 mL/h in presence of 0.01 M $[PA]_0$. Therefore, capacity of limestone and cost benefit analysis was calculated for this flow rate. A preliminary estimation has shown that the process can be adjusted to achieve 1 to 6.6 L/h treated water using a column containing 15 to 100 kg of crushed limestone. Regeneration with NaOH recovers about 75% of the activity of limestone. The regeneration can be repeated up to at least 3 times. Thus, a total volume of about 300 L treated water could be obtained per kg of limestone. This gives a total capacity of 3.84 mg/g of limestone which is much better than the capacity of 0.39 mg/g and 1.01 mg/g reported for limestone alone[14] and for PAELD in batch process[31] and highly competitive with the other low-cost sorbents of fluoride like HAP[14]. The increase in the capacity of limestone is due to increase in the regeneration activity of exhausted limestone compared to the batch mode. In the continuous flow mode, of influent water comes into contact with the limestone surface at a definite flow rate which leads to increase the throughput volume compared to batch mode. Though the interference by $SO_4^{2-}$ ions is slightly greater than that of the batch mode[31], the interference by co-existing $NO_3^-$, $Cl^-$ and $Br^-$ ions is small like the batch mode.

With a cost of limestone as US$ 23 per metric ton and the market price of 85% W/V PA as US$ 0.52 per litre, the cost of limestone and PA per litre of the treated water have been estimated as US$ 0.000115 and 0.0003, respectively. This gives an overall recurring cost for the PAELD in a continuous flow mode to remove fluoride from 5 mg/L to below 1 mg/L as US$ 0.41/m$^3$ of treated water, which is much better than 0.58/m$^3$ estimated for the batch mode. There are scopes for further reduction of the cost as well as improvement of capacity through process optimization including design of column, varying the size of limestone chips.

## Conclusion

Fluoride removal from contaminated water by phosphoric acid-enhanced limestone adsorption is more effective in the continuous-flow mode than in the batch mode reported earlier. The present column technique removes fluoride efficiently from initial 5-10 mg/L to 0.1-1.5 mg/L. The removal increases with decrease in the flow rate. A three stage removal of fluoride, observed with respect to throughput volume, has been attributed to changing degrees of precipitation and adsorption as a function of the throughput volume. The effluent [F$^-$] can also be predicted for a set of fixed conditions of the process. The used exhausted limestone can be regenerated with NaOH to recover 75% activity.

The capacity of limestone in the continuous flow mode has been found to be 3.84 mg/g which is considerably higher than the observed value of 1.01 mg/g in the batch mode[31] and the observed value of 0.39 mg/g by limestone alone[14] in the absence of phosphoric acid.

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